Notes

Assignment of Electronic Spectra of the Platinum(III) Dimer Complexes $[Pt_2(SO_4)_4(H_2O)_2]^{2-}$ and $[Pt_2(HPO_4)_4(H_2O)_2]^{2-}$

Robert Stranger,[*,†] **Sandra C. Nissen,**[‡]
Michael T. Mathieson,[§] **and Trevor G. Appleton**[§]

Department of Chemistry, The Australian National University, Canberra, ACT 0200, Australia, Research School of Chemistry, The Australian National University, Canberra, ACT 0200, Australia, and Department of Chemistry, The University of Queensland, Brisbane, QLD 4072, Australia

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Introduction

Many metals form the dinuclear acetate structure $[M_2(\mu\text{-}O_2CCH_3)_4L_2]$.[1] Perhaps the best known example is the Rh(II) dimer $[Rh_2(\mu\text{-}O_2CCH_3)_4(H_2O)_2]$, which contains a single Rh−Rh bond arising from the d^7d^7 $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*4}$ orbital configuration.[1,2] Although the related d^7d^7 dinuclear complexes of Pt(III) involving bridging sulfate (SO_4^{2-}), hydrogen phosphate (HPO_4^{2-}), and pyrophosphite ($H_2P_2O_5^{2-}$) ligands are well-known, the analogous Pt(III) acetate dimers $[Pt_2(\mu\text{-}O_2CCH_3)_4L_2]^{n+}$ have only recently been reported.[3a]

We recently investigated the electronic structure of the Pt(III) formate dimer $[Pt_2(O_2CH)_4(H_2O)_2]^{2+}$ using the quasi-relativistic Xα-SW method and on the basis of these calculations made tentative assignments for the electronic spectrum of the analogous acetate-bridged dimer $[Pt_2(O_2CCH_3)_4(H_2O)_2]^{2+}$.[3b] Although the X$\alpha$-SW calculations showed that the Pt(III) dimer possessed a metal−metal single bond, analogous to the Rh(II) complex, the energetic ordering of the main metal−metal bonding orbitals was quite different. Furthermore, the calculations revealed that the upper metal-based levels had significant ligand character due to the large stabilization of the Pt(III) 5d orbitals.

From the Xα-SW calculations, the electronic spectrum of $[Pt_2(O_2CCH_3)_4(H_2O)_2]^{2+}$ was predicted[3b] to comprise transitions which were largely ligand-to-metal charge-transfer (LMCT) in nature, in contrast with the spectrum of the corresponding Rh(II) complex where the low-lying transitions are significantly more metal-based.[2,3b,4a−c] It was also noted that, in general, the spectra[5a−c] of the related sulfate- and hydrogen phosphate-bridged dimers $[Pt_2(SO_4)_4L_2]^{4-}$ and $[Pt_2(HPO_4)_4L_2]^{4-}$ (L = H_2O, Cl, Br) were very similar to those of the acetate-bridged complexes, and therefore analogous spectral assignments should apply. This correspondence enabled a rationalization of the previously anomalous MCD reported[5c] for the intense UV band in both the $[Pt_2(SO_4)_4(H_2O)_2]^{2-}$ and $[Pt_2(HPO_4)_4(H_2O)_2]^{2-}$ complexes. Thus, the Xα-SW calculations on $[Pt_2(O_2CH)_4(H_2O)_2]^{2+}$ allow new insights into the nature of the transitions observed in the spectra of the sulfate- and hydrogen phosphate-bridged Pt(III) dimers. The re-examination of the spectra of these complexes in light of these calculations is therefore the subject of this report.

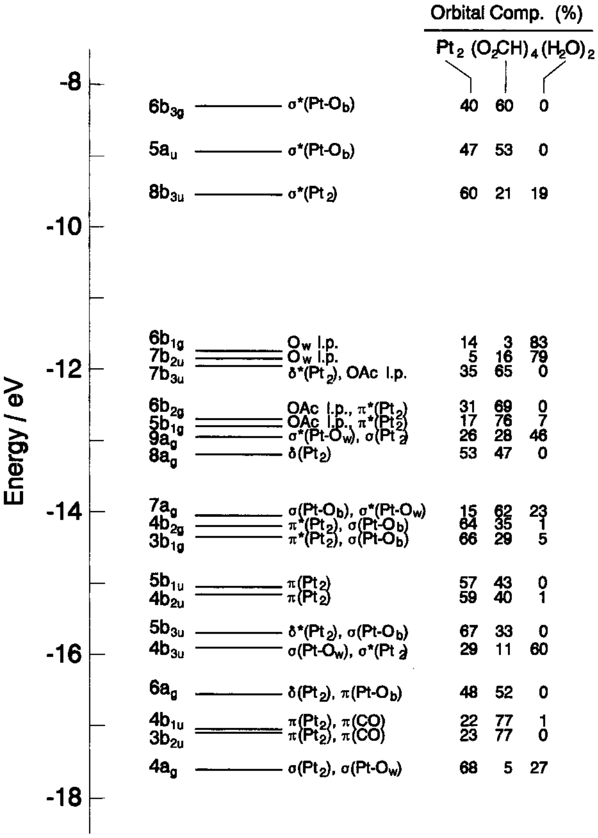

Figure 1. Upper valence energy levels and orbital compositions for $[Pt_2(O_2CH)_4(H_2O)_2]^{2+}$ based on a quasi-relativistic Xα-SW calculation.

Results and Discussion

Since the $[Pt_2O_8L_2]$ dimeric unit is common to $[Pt_2(SO_4)_4(H_2O)_2]^{2-}$, $[Pt_2(HPO_4)_4(H_2O)_2]^{2-}$, and $[Pt_2(O_2CCH_3)_4(H_2O)_2]^{2+}$ and the Pt−Pt distances vary less than 0.1 Å,[3a,6] the upper valence MO energies determined for $[Pt_2(O_2CH)_4(H_2O)_2]^{2+}$ from the quasi-relativistic Xα-SW calculation should serve as a reasonable guide to the electronic structure of all three complexes. Accordingly, to aid in the following discussion, the upper valence energy levels for $[Pt_2(O_2CH)_4(H_2O)_2]^{2+}$ in D_{2h} symmetry are shown in Figure 1 along with an orbital description of each level in terms of diplatinum (Pt_2), bridge-oxygen (O_b), and axial water (O_w) parentage. The deviation from parent D_{4h} symmetry is not significant as evidenced by the small splitting of the (b_{1g},b_{2g}) and (b_{1u},b_{2u}) levels.

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[*] Author to whom correspondence should be addressed.

[†] Department of Chemistry, The Australian National University.

[‡] Research School of Chemistry, The Australian National University.

[§] Department of Chemistry, The University of Queensland.

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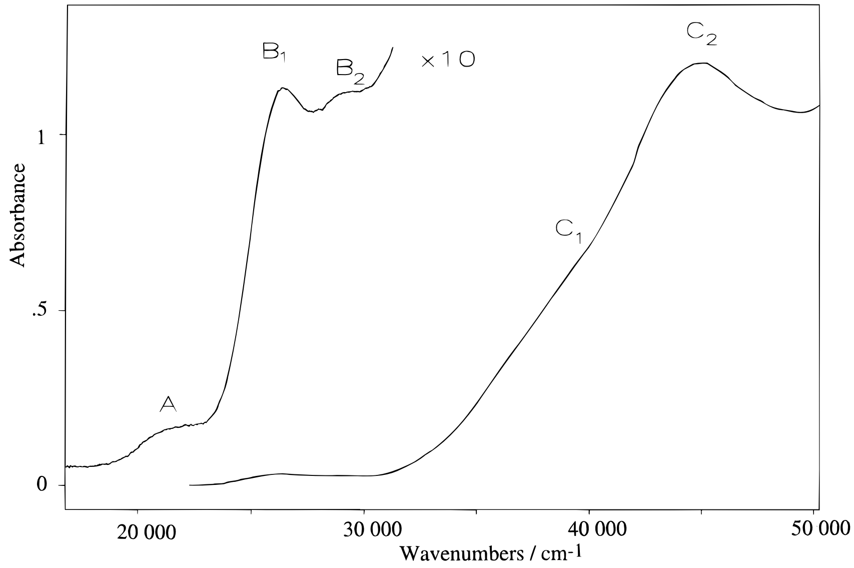

Figure 2. Absorption spectrum of $[Pt_2(SO_4)_4(H_2O)_2]^{2-}$ in aqueous H_2SO_4, pH ~5.

The room temperature absorption spectrum of $[Pt_2(SO_4)_4(H_2O)_2]^{2-}$ shown in Figure 2 is essentially identical to spectra previously reported.[5b,c] The spectrum of the analogous hydrogen phosphate-bridged complex is also very similar.[5a,c] A total of five bands are apparent from the spectrum shown in Figure 2, labeled A, B_1, B_2, C_1, and C_2 in order of increasing energy. Band C_1 is only resolved in the spectrum of the sulfate complex at ~39 000 cm^{-1} while band C_2 is observed in both complexes at around 44 500 cm^{-1}.

Band C_2 has been previously assigned to the $\sigma(O_w,Pt) \rightarrow \sigma^*(Pt_2)$ transition due to the dramatic shift of this band with change in the axial substituents.[5a,b] However, in a later study, both bands C_1 and C_2 were reassigned to $SO_4 \rightarrow \sigma^*(Pt-O_b)$ or $HPO_4 \rightarrow \sigma^*(Pt-O_b)$ charge-transfer transitions on the basis of the observed MCD.[5c] In the absorption spectrum[3b] of $[Pt_2(O_2CCH_3)_4(H_2O)_2]^{2+}$, the intense UV absorption consisted of a single broad band centered at approximately 37 500 cm^{-1}. From the calculated Xα-SW transition state energies and oscillator strengths, a number of transitions were predicted to contribute to this band which were mostly $OAc \rightarrow \sigma^*(Pt-O_b)$ in nature.[3b] In addition, the $\sigma(O_w,Pt) \rightarrow \sigma^*(Pt_2)$ transition (corresponding to $9a_g \rightarrow 8b_{3u}$ in Figure 1), which has partial $\sigma(Pt_2) \rightarrow \sigma^*(Pt_2)$ character, was also predicted to make a significant contribution to this band. This fact, as well as the coincidence of band C_1 in the sulfate-bridged complex with the intense UV band in the acetate-bridged complex, is consistent with band C_1 being assigned to the $\sigma(O_w,Pt) \rightarrow \sigma^*(Pt_2)$ LMCT transition.

Further evidence for the nature of band C_1 comes from a comparison of the $\sigma(L,Pt) \rightarrow \sigma^*(Pt_2)$ transition energies in the axially substituted adducts of the sulfate- and pop (pop = $P_2O_5H_2^{2-}$)-bridged complexes.[5b,c,7a−f] The observed transition energies for the two series are plotted in Figure 3. The significant linear correlation observed between these two systems argues favorably for the assignment of band C_1 to the $\sigma(O_w,Pt) \rightarrow \sigma^*(Pt_2)$ transition in the sulfate complex.

Band C_2 at approximately 44 500 cm^{-1} in both the sulfate and hydrogen phosphate complexes is now more compatible with either $SO_4 \rightarrow \sigma^*(Pt-O_b)$ or $HPO_4 \rightarrow \sigma^*(Pt-O_b)$ LMCT transitions. These transitions are consistent with the negative MCD A term observed for the intense UV band[5c] and also explain why the MCD is centered around 45 000 cm^{-1} rather than band C_1 lying to lower energy at ~39 000 cm^{-1}.

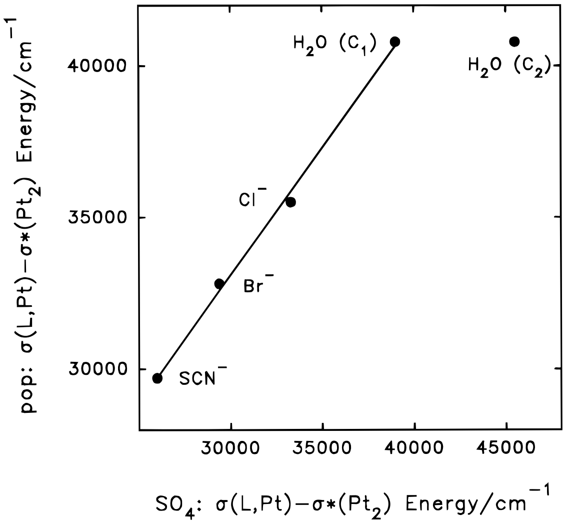

Figure 3. Plot of the $\sigma(L,Pt) \rightarrow \sigma^*(Pt_2)$ transition energies in $[Pt_2(SO_4)_4L_2]^{n-}$ and $[Pt_2(P_2O_5H_2)_4L_2]^{n-}$ (L = OH_2, Cl, Br, SCN) complexes.

Band B_1, observed at ~26 000 cm^{-1} in the sulfate- and hydrogen phosphate bridged complexes, has been previously assigned[5a−c] to the $\pi^*(Pt_2) \rightarrow \sigma^*(Pt_2)$ transition consistent with the positive MCD A term observed for this band.[5c] However, our Xα-SW calculation on the formate-bridged complex indicates that the upper $\pi^*(Pt_2)$ level, corresponding to the $5b_{1g}$ and $6b_{2g}$ orbitals in Figure 1, has significant (~70%) bridge character, in marked contrast to the upper $\pi^*(Rh_2)$ level in $Rh(O_2CH)_4(H_2O)_2$, which has around 80% metal character.[2,3b] This implies that transitions from these orbitals to the $\sigma^*(Pt_2)$ $8b_{3u}$ level are more charge transfer in nature than metal-based and thus are more appropriately assigned as $O_b \rightarrow \sigma^*(Pt_2)$ rather than $\pi^*(Pt_2) \rightarrow \sigma^*(Pt_2)$. The MCD observed for band B_1 is also consistent with this assignment. Further evidence for the assignment of band B_1 in the sulfate-, hydrogen phosphate-, and acetate-bridged Pt(III) dimer complexes comes from the significant lower energy shift of this band[3a,b,5a−c] as the axial

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ligands are changed from H_2O to Cl and Br, consistent with the $\sigma^*(Pt_2)$ character of the acceptor orbital.

Band B_2, observed between 28 500 and 30 000 cm^{-1} in the sulfate- and hydrogen phosphate-bridged complexes, occurs as a very weak absorption to the higher energy side of band B_1 but is not resolved in the spectrum of $[Pt_2(O_2CCH_3)_4(H_2O)_2]^{2+}$. This transition was previously assigned[5a−c] to the electric-dipole forbidden $\delta^*(Pt_2) \rightarrow \sigma^*(Pt_2)$ transition on the basis that the $\delta^*(Pt_2)$ level was thought to lie below the $\pi^*(Pt_2)$ level due to the shorter Pt−Pt distances in both the sulfate- and hydrogen phosphate-bridged complexes compared to the pyrophosphite-bridged complexes. However, from the upper valence levels of $[Pt_2(O_2CH)_4(H_2O)_2]^{2+}$ shown in Figure 1, the $\delta^*(Pt_2)$ ($7b_{3u}$) level is seen to lie above the upper $\pi^*(Pt_2)$ ($5b_{1g}$,$6b_{2g}$) levels, and thus the $\delta^*(Pt_2) \rightarrow \sigma^*(Pt_2)$ transition should lie below band B_1. Since the Pt−Pt distances are similar in $[Pt_2(O_2CCH_3)_4(H_2O)_2]^{2+}$, $[Pt_2(SO_4)_4(H_2O)_2]^{2-}$, and $[Pt_2(HPO_4)_4(H_2O)_2]^{2-}$ dimers, the same argument should also hold for the latter two complexes. On the basis of the Xα-SW calculated transition energies[3b] for $[Pt_2(O_2CH)_4(H_2O)_2]^{2+}$, the $\delta(Pt_2) \rightarrow \sigma^*(Pt_2)$ ($8a_g \rightarrow 8b_{3u}$) transition is a very strong possibility for the assignment of band B_2 as it is predicted to lie slightly to higher energy of band B_1 at ∼29 700 cm^{-1}. Furthermore, the calculated oscillator strength of this transition is very low (<0.001), in agreement with the very weak intensity observed for band B_2.

Band A, observed between 20 000 and 21 500 cm^{-1} in the sulfate- and hydrogen phosphate-bridged complexes, has been previously assigned to the corresponding spin-triplet $\pi^*(Pt_2) \rightarrow \sigma^*(Pt_2)$ transition due to the very weak intensity and emission observed for this excited state.[5a,b] Given that the upper $\pi^*(Pt_2)$ level is predominantly O(bridge) in character, band A is now more correctly assigned as the spin-triplet $O_b \rightarrow \sigma^*(Pt_2)$ transition.

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