

Magnetic Circular Dichroism Spectra for the Binuclear $\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4^{4-}$ Ion and the Related $\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4\text{Cl}_2^{4-}$ and $\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4\text{Br}_2^{4-}$ Ions

HUSEYIN ISCI¹ and W. ROY MASON*

Received August 22, 1984

Magnetic circular dichroism (MCD) spectra are reported for $\text{Pt}_2(\text{pop})_4^{4-}$, $\text{Pt}_2(\text{pop})_4\text{Cl}_2^{4-}$, and $\text{Pt}_2(\text{pop})_4\text{Br}_2^{4-}$ (pop = $\text{P}_2\text{O}_5\text{H}_2^{2-}$) in aqueous solution. A positive A term is observed for the band at $2.21 \mu\text{m}^{-1}$ and a strong negative B term is found for the band at $2.7 \mu\text{m}^{-1}$ for $\text{Pt}_2(\text{pop})_4^{4-}$. These MCD terms are consistent with transitions to the $E_u(^3A_{2u})$ and $A_{2u}(^1A_{2u})$ states, respectively, of the lowest $d\sigma^*p\sigma$ excited configuration. The MCD for $\text{Pt}_2(\text{pop})_4^{4-}$ above $3.0 \mu\text{m}^{-1}$ consists largely of B terms with a strong positive term at $4.13 \mu\text{m}^{-1}$ and a strong negative term at $4.47 \mu\text{m}^{-1}$. The MCD at $4.13 \mu\text{m}^{-1}$ is also found to contain a weaker positive A term. This region is interpreted in terms of higher $dp\sigma$ configurations. The intense bands at $3.50 \mu\text{m}^{-1}$ for $\text{Pt}_2(\text{pop})_4\text{Cl}_2^{4-}$ and $3.23 \mu\text{m}^{-1}$ for $\text{Pt}_2(\text{pop})_4\text{Br}_2^{4-}$ both exhibit strong negative B terms, consistent with the $d\sigma \rightarrow d\sigma^*$ transition to the $A_{2u}(^1A_{2u})$ state. At lower energy ($2.9 \mu\text{m}^{-1}$ for $\text{Pt}_2(\text{pop})_4\text{Cl}_2^{4-}$ and $2.8 \mu\text{m}^{-1}$ for $\text{Pt}_2(\text{pop})_4\text{Br}_2^{4-}$) a prominent positive A term is observed for both ions and is interpreted as the $d\pi^* \rightarrow d\sigma^*$ transition to the $E_u(^1E_u)$ state. A strong negative MCD band near $4.7 \mu\text{m}^{-1}$ associated with the absorption near $4.6 \mu\text{m}^{-1}$ is also observed for both $\text{Pt}_2(\text{pop})_4\text{X}_2^{4-}$ ions. The electronic states of the dinuclear Pt_2P_8 cluster are discussed and correlated with related states of mononuclear PtP_4 complexes.

Introduction

The binuclear diplatinum(II) ion $\text{Pt}_2(\text{pop})_4^{4-}$ (pop = $\text{P}_2\text{O}_5\text{H}_2^{2-}$) has attracted considerable interest because its structure consists of two square-planar PtP_4 units linked together face to face, giving an eclipsed Pt_2P_8 cluster with a relatively short Pt-Pt distance (2.925 \AA).² Even though the diamagnetic d^8d^8 ground-state electron configuration gives rise to filled bonding $d\sigma$ ($1a_{1g}$, D_{4h}) and antibonding $d\sigma^*$ ($1a_{2u}$) orbitals, the short Pt-Pt distance indicates significant interaction between the Pt(II) centers.³ This interaction is reflected in a number of interesting spectroscopic and redox features.⁴⁻¹³ For example, one of the most striking features of $\text{Pt}_2(\text{pop})_4^{4-}$, both in solution and in solid compounds, is an intense green luminescence, which is observed even at room temperature upon irradiation with UV light. The luminescence has been extensively studied^{5-7,9,13} and has been characterized as emission from states of the $d\sigma^*p\sigma$, ($1a_{2u}$)($2a_{1g}$), excited configuration with fluorescence from the $^1A_{2u}$ state ($2.46 \mu\text{m}^{-1}$, $\tau < 2\text{ ns}$) and phosphorescence from the E_u and A_{1u} spin-orbit components of the $^3A_{2u}$ state ($1.93 \mu\text{m}^{-1}$, $\tau \sim 10 \mu\text{s}$ at room temperature). The two lowest energy bands in the absorption spectrum correspond to the excitation spectrum for the emission and therefore have been assigned to the transitions $^1A_{1g} \rightarrow ^3A_{2u}$ ($2.21 \mu\text{m}^{-1}$, ϵ $110 \text{ M}^{-1} \text{ cm}^{-1}$) and $^1A_{1g} \rightarrow ^1A_{2u}$ ($2.72 \mu\text{m}^{-1}$, ϵ $3.4 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$), respectively. Further, when $\text{Pt}_2(\text{pop})_4^{4-}$ is treated with halogen, binuclear dihaloplatinum(III) $\text{Pt}_2(\text{pop})_4\text{X}_2^{4-}$ complexes are formed by oxidative addition.¹⁴ These complexes retain the Pt_2P_8 cluster and also contain axial Pt-X bonds and a Pt-Pt single bond. The

Pt-Pt distance shortens (to 2.65 \AA in $\text{Pt}_2(\text{pop})_4\text{Cl}_2^{4-15}$), consistent with the two $d\sigma^*$ electrons of $\text{Pt}_2(\text{pop})_4^{4-}$ being transferred to the halogen atoms, giving the diamagnetic d^7d^7 ground-state configuration ($d\sigma$)². The lowest energy bands in the electronic spectra of the $\text{Pt}_2(\text{pop})_4\text{X}_2^{4-}$ complexes have been ascribed to excitations to the empty $d\sigma^*$ orbital.¹⁴

As a result of our recent study of electronic absorption and magnetic circular dichroism (MCD) spectra of some related planar PtP_4 chromophores,¹⁶ we quite naturally became interested in their relationship to the binuclear complexes. While previous studies of the $\text{Pt}_2(\text{pop})_4^{4-}$ ion have focused on the lowest energy excited states of the $d\sigma^*p\sigma$ configuration responsible for the emission, the higher energy excited configurations and the resulting states have received much less attention even though several prominent absorption bands are observed above $3.0 \mu\text{m}^{-1}$ in the UV region. An interpretation of this higher energy region of the spectrum based on some spin-orbit calculations was presented recently.¹⁷ While such calculations are frequently helpful, they are sensitive to the energy of the zero-order states. Therefore, to provide some additional spectroscopic information for the placement of the higher energy excited states of the $\text{Pt}_2(\text{pop})_4^{4-}$ ion and to correlate these states and those of the related $\text{Pt}_2(\text{pop})_4\text{X}_2^{4-}$ ions with the states of mononuclear PtP_4 complexes, we report here some MCD spectra for $\text{Pt}_2(\text{pop})_4^{4-}$, $\text{Pt}_2(\text{pop})_4\text{Cl}_2^{4-}$, and $\text{Pt}_2(\text{pop})_4\text{Br}_2^{4-}$ in aqueous solution. The MCD in the region of the two lowest energy bands of $\text{Pt}_2(\text{pop})_4^{4-}$ is in accord with and complements the results of the previous absorption,⁵⁻⁷ emission,^{5-7,9} and polarization ratio¹³ studies.

Experimental Section

The compounds $\text{K}_4[\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4] \cdot 2\text{H}_2\text{O}$, $\text{K}_4[\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4\text{Cl}_2] \cdot 2\text{H}_2\text{O}$, and $\text{K}_4[\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4\text{Br}_2] \cdot 2\text{H}_2\text{O}$ were prepared by literature methods.^{2,6,14,15} Absorption spectra for aqueous solutions of these compounds followed Beer's law to within experimental error and were in agreement with previous reports of band positions and absorptivities.^{5,6,14} Aqueous solutions of $\text{Pt}_2(\text{pop})_4^{4-}$ were prepared with O_2 -free water. Spectral measurements were made at room temperature by means of a Cary 1501 spectrophotometer and a computer-controlled MCD spectrometer that allows measurement of the absorption spectra simultaneously along the same light path as the MCD spectra.¹⁸ The field strength for the MCD measurements was 7.0 T (Oxford Instruments SM2-7 superconducting magnet system, equipped with a room-temperature bore).

Results and Discussion

Absorption and MCD Spectra. Figures 1 and 2 present the absorption and MCD spectra of the $\text{Pt}_2(\text{pop})_4^{4-}$ and $\text{Pt}_2(\text{pop})_4\text{Cl}_2^{4-}$

- (1) Present address: Department of Chemistry, Middle East Technical University, Ankara, Turkey.
- (2) Filomiena Dos Remedios Pinto, M. A.; Sadler, P. J.; Neidle, S.; Sanders, M. R.; Subbiah, A.; Kuroda, R. *J. Chem. Soc., Chem. Commun.* **1980**, 13.
- (3) (a) Stein, P.; Dickson, M. K.; Roundhill, D. M. *J. Am. Chem. Soc.* **1983**, *105*, 3489. (b) Che, C.-M.; Butler, L. G.; Gray, H. B.; Crooks, R. M.; Woodruff, W. H. *J. Am. Chem. Soc.* **1983**, *105*, 5492.
- (4) Sperline, R. P.; Dickson, M. K.; Roundhill, D. M. *J. Chem. Soc., Chem. Commun.* **1977**, 62.
- (5) Fordyce, W. A.; Brummer, J. G.; Crosby, G. A. *J. Am. Chem. Soc.* **1981**, *103*, 7061.
- (6) Che, C.-M.; Butler, L. G.; Gray, H. B. *J. Am. Chem. Soc.* **1981**, *103*, 7796.
- (7) Rice, S. F.; Gray, H. B. *J. Am. Chem. Soc.* **1983**, *105*, 4571.
- (8) Dickson, M. K.; Pettee, S. K.; Roundhill, D. M. *Anal. Chem.* **1981**, *53*, 2159.
- (9) Markert, J. T.; Clements, D. P.; Corson, M. R.; Nagle, J. K. *Chem. Phys. Lett.* **1983**, *97*, 175.
- (10) Heuer, W. B.; Totten, M. D.; Rodman, G. S.; Hebert, E. J.; Tracy, H. J.; Nagle, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 1163.
- (11) Bryan, S. A.; Dickson, M. K.; Roundhill, D. M. *J. Am. Chem. Soc.* **1984**, *106*, 1882.
- (12) Alexander, K. A.; Stein, P.; Hedden, D. B.; Roundhill, D. M. *Polyhedron* **1983**, *2*, 1389.
- (13) Parker, W. L.; Crosby, G. A. *Chem. Phys. Lett.* **1984**, *105*, 544.
- (14) Che, C.-M.; Schaefer, W. P.; Gray, H. B.; Dickson, M. K.; Stein, P. B.; Roundhill, D. M. *J. Am. Chem. Soc.* **1982**, *104*, 4253.

- (15) Che, C.-M.; Herstein, F. H.; Schaefer, W. P.; Marsh, R. E.; Gray, H. B. *J. Am. Chem. Soc.* **1983**, *105*, 4604.
- (16) Solar, J. M.; Ozkan, M. A.; Isci, H.; Mason, W. R. *Inorg. Chem.* **1984**, *23*, 758.
- (17) Shimizu, Y.; Tanaka, Y.; Azumi, T. *J. Phys. Chem.* **1984**, *88*, 2423.
- (18) Mason, W. R. *Anal. Chem.* **1982**, *54*, 646.

Table I. Spectral Data (Aqueous Solution)

band	absorption		MCD $\bar{\nu}$, μm^{-1} ($\Delta\epsilon_M$, $\text{M}^{-1} \text{cm}^{-1} \text{T}^{-1}$)	assign state, confign
	λ_{max} , nm	$\bar{\nu}$, μm^{-1} (ϵ , $\text{M}^{-1} \text{cm}^{-1}$)		
$\text{K}_4[\text{Pt}_2(\text{pop})_4] \cdot 2\text{H}_2\text{O}$				
I	452	2.21 (110)	$b \begin{cases} 2.15 (-0.142) \\ 2.29 (0) \\ 2.36 (+0.018) \end{cases}$	$\text{E}_u(^3\text{A}_{2u}), (1a_{2u})(2a_{1g})$
II	369	2.71 (30 900)	2.73 (-1.84)	$\text{A}_{2u}(^1\text{A}_{2u}), (1a_{2u})(2a_{1g})$
III	305	3.28 (1000) ^a	3.21 (+0.31)	$\text{E}_u(^3\text{E}_u), (e_u)^3(2a_{1g})$
IV	270	3.71 (1500)	3.45 (-0.21)	$\text{A}_{2u}(^3\text{E}_u), (e_u)^3(2a_{1g})$
			3.74 (+0.32)	$\text{E}_u(^3\text{B}_{1u}), (b_{1u})(2a_{1g})$
V	245	4.08 (2930)	$b \begin{cases} 3.93 (-0.01) \\ 4.13 (+1.62) \end{cases}$	$\text{E}_u(^1\text{E}_u), (e_u)^3(2a_{1g})$
VI	220	4.55 (10 700) ^a	4.47 (-1.42)	$\text{A}_{2u}(^1\text{A}_{2u}), (1a_{1g})(2a_{2u})$
$\text{K}_4[\text{Pt}_2(\text{pop})_4\text{Cl}_2] \cdot 2\text{H}_2\text{O}$				
I	385	260 (4300) ^a	2.46 (+0.48)	$\text{E}_u, \text{A}_{2u}(^3\text{E}_u), (e_g)^3(1a_{2u})$
II	347	2.88 (7600)	2.78 (-0.91)	$\text{E}_u(^3\text{A}_{2u}), (1a_{1g})(1a_{2u})$
			2.93 (0)	$\text{E}_u(^1\text{E}_u), (e_g)^3(1a_{2u})$
III	286	3.50 (47 000)	3.15 (+1.63)	$\text{A}_{2u}(^1\text{A}_{2u}), (1a_{1g})(1a_{2u})$
			3.51 (-2.18)	
IV	216	4.63 (49 000)	4.76 (-5.8)	
$\text{K}_4[\text{Pt}_2(\text{pop})_4\text{Br}_2]$				
II	358	2.79 (10 400)	2.73 (-1.67)	$\text{E}_u(^3\text{A}_{2u}), (1a_{1g})(1a_{2u})$
			2.84 (0)	$\text{E}_u(^1\text{E}_u), (e_g)^3(1a_{2u})$
III	310	3.23 (55 000)	2.97 (+2.55)	$\text{A}_{2u}(^1\text{A}_{2u}), (1a_{1g})(1a_{2u})$
IV	217	4.60 (35 000)	3.28 (-3.68)	
			4.67 (-4.5)	

^a Shoulder. ^b A Term.

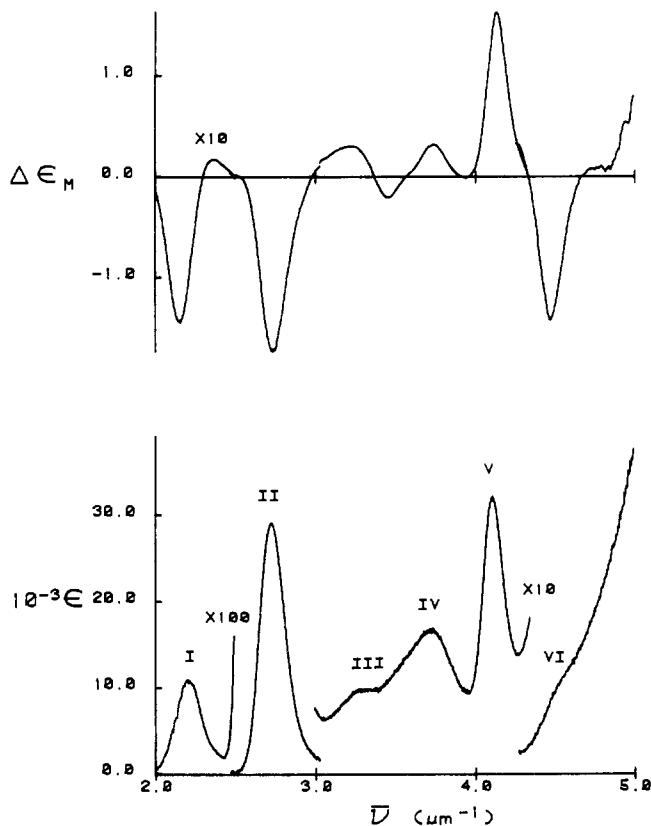


Figure 1. Electronic absorption (lower curves) and MCD (upper curves) spectra for $\text{K}_4[\text{Pt}_2(\text{pop})_4] \cdot 2\text{H}_2\text{O}$ in water. Note that the MCD scale has been expanded 10-fold from 2.0 to 2.5 μm^{-1} ; similarly the absorptivity scales have been expanded 100-fold from 2.0 to 2.5 μm^{-1} and 10-fold from 3.0 to 4.3 μm^{-1} . $\Delta\epsilon_M$ has units of $(\text{M cm T})^{-1}$.

ions, respectively; the spectra for $\text{Pt}_2(\text{pop})_4\text{Br}_4^{4-}$ were of comparable quality. Quantitative spectral data are summarized in Table I.

The bands in the absorption spectrum of $\text{Pt}_2(\text{pop})_4^{4-}$ above 3.0 μm^{-1} (bands III–V) occur in the same energy region as intense

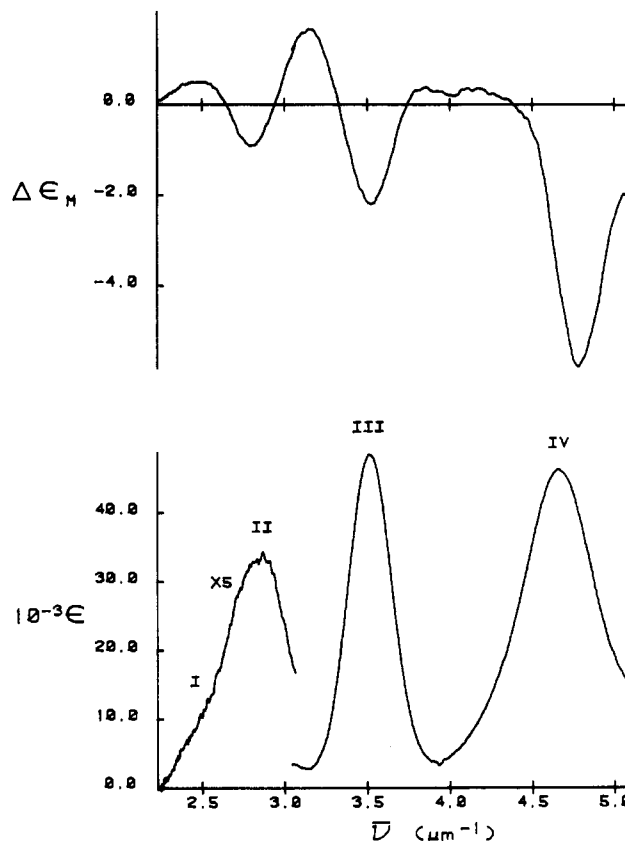


Figure 2. Electronic absorption (lower curves) and MCD (upper curve) spectra for $\text{K}_4[\text{Pt}_2(\text{pop})_4\text{Cl}_2]$ in water. Note that the absorptivity scale has been expanded 5-fold from 1.7 to 3.0 μm^{-1} . $\Delta\epsilon_M$ has units of $(\text{M cm T})^{-1}$.

bands for mononuclear PtP_4 complexes.¹⁶ Since we have observed, and it has been reported by others,^{2,4,12} that the $\text{Pt}_2(\text{pop})_4^{4-}$ ion undergoes a hydrolytic cleavage reaction that apparently gives a mononuclear $\text{Pt}(\text{II})$ product, the possibility that some portion of the absorption above 3.0 μm^{-1} might be due to hydrolysis

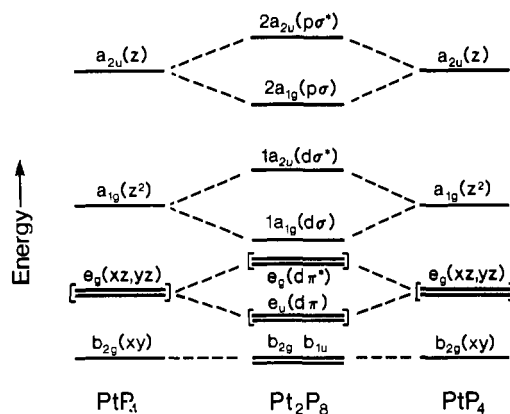
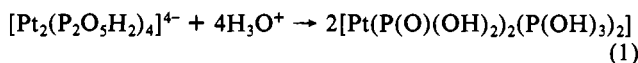


Figure 3. Simplified MO energy level scheme showing the correlation between the levels of the binuclear Pt₂P₈ cluster and a mononuclear PtP₄ complex.

products was investigated. A sample of Pt₂(pop)₄⁴⁻ in 0.10 M HClO₄ was heated in a hot water bath at 90° C for 5 min. Under these conditions the hydrolysis reaction proceeded cleanly and completely with no trace of Pt₂(pop)₄⁴⁻ remaining as judged by the complete absence of the intense band at 2.71 μm⁻¹ (band II) characteristic of the binuclear complex. The product UV spectrum (band, $\bar{\nu}$, μm⁻¹ (ε, M⁻¹ cm⁻¹) (assuming a mononuclear complex) I, 3.29 (491); II, 3.81 (8050); III, 4.18 (2780)) and MCD spectrum (positive *A* term for band I, a strong negative *B* term (Δε_M = 2.7 M⁻¹ cm⁻¹ T⁻¹) for band II, and a broad positive *B* term in the region of band III) were significantly different from those for Pt₂(pop)₄⁴⁻ (Table I; Figure 1). For example, the strong negative *B* term at 3.81 μm⁻¹ for the hydrolysis product can be compared with a positive MCD near this energy in the region of band IV for the binuclear complex. Thus, bands III and IV in Figure 1 are reasonably attributed to transitions of the Pt₂(pop)₄⁴⁻ ion. It is interesting to note that the UV and MCD spectra for the hydrolysis product are nearly the same as for the dimethyl phosphite dimethyl phosphito complex [Pt(P(O)(OMe)₂(P(OH)(OMe)₂)₂] studied earlier¹⁶ (UV bands at 3.24 (520), 3.73 (7900), and 4.10 (3100)). This suggests that in acid solution the hydrolytic reaction gives the related neutral complex in eq 1. The same formulation for the hydrolysis product was suggested earlier on the basis of some ³¹P NMR results.¹²



Molecular Orbitals, Excited States, and MCD Terms.¹⁹ A simplified MO energy level diagram that will be helpful in visualizing the various excited configurations for the binuclear complexes is given in Figure 3. *D*_{4h} symmetry is assumed for both Pt₂(pop)₄⁴⁻ and Pt₂(pop)₄X₂⁴⁻ with the *z* axis taken along the 4-fold Pt-Pt axis. The relevant levels of the mononuclear PtP₄ complex that serve as a basis for the levels of the Pt₂P₈ cluster are also shown in Figure 3. In the d⁸d⁸ Pt₂(pop)₄⁴⁻ ion, the highest occupied level is 1a_{2u} and the diamagnetic ground state is ¹A_{1g}. The two dσ* electrons of 1a_{2u} are not present for the d⁷d⁷ Pt₂(pop)₄X₂⁴⁻ ions, but the ground state remains diamagnetic and ¹A_{1g}. The halogen levels of the dihalo complexes are expected to be more stable than the MO's derived from the Pt 5d orbitals and thus are not expected to be involved in the lowest energy excited configurations. The relative stability of the occupied orbitals of Figure 3 may also change slightly on oxidation from Pt(II) to Pt(III); both the dσ and the dπ orbitals are expected to have some halogen contribution. The scheme in Figure 3 should still be suitable for the discussion here.

It is clear from Figure 3 that the lowest energy excited configuration for Pt₂(pop)₄⁴⁻ will involve 2a_{1g}(pσ) and 2a_{2u}(pσ*)

Table II. Excited Configurations and States

excited config ^a	no spin-orbit coupling	spin-orbit states ^b	MCD term sign	
			<i>A</i>	<i>B</i> ^c
Pt ₂ (pop) ₄ ⁴⁻				
(1a _{2u})(2a _{1g}) or (1a _{1g})(2a _{2u})		¹ A _{2u}		-
		³ A _{2u}	E _u	-
(e _g) ³ (2a _{1g}) or (e _g) ³ (2a _{2u})		¹ E _u	E _u	+
		³ E _u	E _u	+
			A _{2u}	-
(b _{1u})(2a _{1g}) or (b _{2g})(2a _{2u})		¹ B _{1u}		
		³ B _{1u}	E _u	+
Pt ₂ (pop) ₄ X ₂ ⁴⁻				
(e _g) ³ (1a _{2u}) or (e _u)(2a _{1g})		¹ E _u	E _u	+
		³ E _u	E _u	+
(a _{1g})(1a _{2u}) or (a _{1g})(2a _{2u})		¹ A _{2u}	A _{2u}	
		³ A _{2u}	E _u	+
(b _{2g})(1a _{2u}) or (b _{1u})(2a _{1g})		¹ B _{1u}		
		³ B _{1u}	E _u	-

^a Filled orbitals omitted. ^b Allowed states. ^c Sign sensitive to relative orbital energy (see text). Energy order assumed: E_u(³A_{2u}) < A_{2u}(¹A_{2u}) < E_u(³E_u) < A_{2u}(³E_u) < E_u(³B_{1u}) < E_u(¹E_u). See ref 16 and 20.

orbitals, while for the Pt₂(pop)₄X₂⁴⁻ ions configurations involving 1a_{2u}(dσ*) will lie lowest. Allowed excited states for electric dipole transitions in both cases are limited to *z*-polarized A_{2u} and *xy*-polarized E_u states, but because of strong Pt spin-orbit coupling, transitions to A_{2u} or E_u states of triplet parentage can gain appreciable intensity. The nondegenerate A_{2u} states can only exhibit *B* terms in the MCD, which result from magnetic mixing with E_u states. Degenerate E_u states however can give rise to *A* terms, which result from Zeeman splitting of the degenerate levels and also to *B* terms from magnetic mixing with either A_{2u} states or other E_u states (*C* terms, of course, will be absent for these diamagnetic complexes).

Two sets of excited states can be visualized for Pt₂(pop)₄⁴⁻: one from configurations involving the 2a_{1g}(pσ) orbital and 1a_{2u}, e_u, or b_{1u}; and one from configurations involving the 2a_{2u}(pσ*) orbital and 1a_{1g}, e_g, or b_{2g}. These configurations and their allowed states are collected in Table II. The symmetries of both sets of states, which are the same, are also the same as for the states of a mononuclear PtP₄ complex from configurations of the a_{2u}(*z*) orbital and a_{1g}(*z*²), e_g(*xz*, *yz*), and b_{2g}(*xy*). It is important to note that since the 2a_{1g} and 2a_{2u} orbitals are different, the two sets of states for Pt₂(pop)₄⁴⁻ will not be intermixed either by spin-orbit coupling or by the external magnetic field in the MCD measurements. Therefore, to a good approximation the excited spin-orbit states expected for the binuclear complex and the *A* and *B* terms associated with them in the MCD can be determined by the same considerations used earlier for mononuclear MP₄ [M = Ir(I), Pt(II)] complexes.^{16,20} Thus, the *A* term sign for each of the spin-orbit E_u states of each set can be determined in the standard way by approximating the one-electron MO's as pure 5d or 6p atomic orbitals of the Pt centers and retaining only one-centered integrals (see ref 20 for details). The signs of the *B* terms can also be predicted since the states of the 2a_{1g} or 2a_{2u} configurations (Table II), like those of a_{2u}(*z*) configurations of MP₄, lie relatively close in energy compared to all other A_{2u} or E_u states that involve these orbitals. This feature allows the summation over all states that occurs in the *B* term expressions¹⁹ to be simplified because of the inverse dependence on the energy difference between the states that can interact in the presence of the magnetic field. Contributions from A_{2u} or E_u states outside of the 2a_{1g} or 2a_{2u} configurations of Table II are assumed to be too small to be significant. The *B* term signs do depend upon the relative energy of the A_{2u} and E_u states within the 2a_{1g} or 2a_{2u} configurations.

(19) For a review of MCD spectroscopy together with the standard conventions adopted here see: Piepho, S. B.; Schatz, P. N. "Group Theory in Spectroscopy with Applications to Magnetic Circular Dichroism"; Wiley-Interscience: New York, 1983.

(20) Geoffroy, G. L.; Isci, H.; Litrenti, J.; Mason, W. R. *Inorg. Chem.* 1977, 16, 1950.

The B term signs for the spin-orbit states of each set given in Table II were determined by assuming the energy ordering $E_u(^3A_{2u}) < A_{2u}(^1A_{2u}) < E_u(^3E_u) < A_{2u}(^0E_u) < E_u(^3B_{1u}) < E_u(^1E_u)$ (see ref 20 for details). Except for the minor change in the relative order of $E_u(^1E_u)$ and $E_u(^3B_{1u})$, this order is the same as used previously for B term calculations for a number of Ir(I) and Pt(II) MP_4 complexes.^{16,20}

The lowest energy excited configurations expected for the $Pt_2(pop)_4X_2^{4-}$ ions are also listed in Table II, together with the A term signs predicted for each E_u state. The calculation of B term signs was not carried out for the $Pt_2(pop)_4X_2^{4-}$ ions. In contrast to $Pt_2(pop)_4^{4-}$ where the excited states of configurations involving the same virtual orbital were all relatively close in energy, there will be A_{2u} and E_u excited states at higher energy due to ligand-to-metal charge transfer (LMCT) from the halogen to the $1a_{2u}$, $2a_{1g}$, and $2a_{2u}$ orbitals in $Pt_2(pop)_4X_2^{4-}$. These LMCT states can contribute to the B terms for the metal-localized transitions of Table II, and calculations excluding the LMCT states are not expected to be reliable.

Spectral Interpretation. $Pt_2(pop)_4^{4-}$. The MCD spectra (Figure 1) for the two lowest energy bands of $Pt_2(pop)_4^{4-}$ (band I at $2.21 \mu m^{-1}$; band II at $2.7 \mu m^{-1}$) are consistent with the excited-state assignments given earlier from absorption and emission studies.^{5-7,9,13} The strong negative B term observed for the intense band II is predicted for the transition to the $A_{2u}(^1A_{2u})$ state of the lowest energy $(1a_{2u})(2a_{1g})$ configuration. The largest contribution to the B term for the $A_{2u}(^1A_{2u})$ state will be from the higher energy $E_u(^1E_u)$ state of $(e_u)^3(2a_{1g})$, the only E_u state of predominantly singlet parentage from a configuration involving the same $p\sigma$ $2a_{1g}$ orbital. This point is important to the discussion of higher energy states (see below). In contrast to band II, the MCD for band I is unsymmetrical and dominated by the expected negative B term. A change of sign for $\Delta\epsilon_M$ near the band maximum, however, is apparent in Figure 1, and a careful moment analysis¹⁹ of the spectra in the region of band I shows a significant positive A term²¹ consistent with the $E_u(^3A_{2u})$ assignment. Finally, a transition to the highly forbidden $A_{1u}(^3A_{2u})$ state, which should also be present in the region of band I, is assumed to be too weak to be observed in either the absorption or MCD spectra.

The MCD above $3.0 \mu m^{-1}$ is dominated by a number of B terms. The two strongest features are associated with band V ($4.08 \mu m^{-1}$) and band VI (shoulder at $4.55 \mu m^{-1}$). The strong positive MCD for band V has a maximum slightly, but significantly, higher in energy than the absorption maximum, suggesting the presence of a weak A term. Since band V is well separated from the other bands in the spectrum, a moment analysis was deemed feasible; the results of the analysis showed a definite positive A term,²² indicating that band V corresponds to a transition to an E_u state. Two possibilities within the configurations involving the $2a_{1g}$ orbital present themselves. Transitions to $E_u(^3E_u)$ and $E_u(^1E_u)$, both of $(e_u)^3(2a_{1g})$, are expected to exhibit positive A terms and positive B terms. An assignment to $E_u(^1E_u)$ is strongly suggested however, on the basis of the magnitude of the B term for band V. Theory predicts that two separated states, which interact in the presence of the field, will give rise to B terms of opposite sign and equal magnitude located at their respective transition energies.¹⁹ Therefore, the strong negative B term of band II for $A_{2u}(^1A_{2u})$ discussed above requires a positive B term of comparable magnitude for the $E_u(^1E_u)$ counterpart. The B term for band V presents the lowest energy positive term of comparable magnitude to that of band II. An assignment of band V to the transition to $E_u(^3B_{1u})$ of $(b_{1u})(2a_{1g})$ can be excluded because the A term is the wrong sign.

The term assignment for the strong negative MCD for band VI is more difficult because the absorption is a poorly defined shoulder. However, the MCD is fairly symmetrical and appears

to flatten on the high-energy side of the band near zero $\Delta\epsilon_M$ before increasing at higher energy, and thus the band resembles a negative B term. Because of its magnitude it is unlikely that it is associated with a state of predominantly triplet parentage such as $A_{2u}(^3E_u)$, $(e_u)^3(2a_{1g})$; $E_u(^3B_{1u})$, $(b_{1u})(2a_{1g})$; or $E_u(^3A_{2u})$, $(1a_{1g})(2a_{2u})$. More likely, band VI corresponds to the transition to $A_{2u}(^1A_{2u})$ of the $(1a_{1g})(2a_{2u})$ $d\sigma\sigma^*$ configuration; the negative B term would be analogous to that of band II for the $A_{2u}(^1A_{2u})$ of the $(1a_{2u})(2a_{1g})$ $d\sigma^*p\sigma$ configuration.

The MCD from 3.0 to $3.8 \mu m^{-1}$ is weaker and appears to consist of positive B terms at 3.21 and $3.74 \mu m^{-1}$ separated by a negative B term at $3.45 \mu m^{-1}$. The interpretation in this region is complicated by the overlapping absorptions of bands III and IV. Band IV is also noticeably broad on its low-energy side, suggesting one or more additional unresolved bands. The relative weakness of both the MCD and absorption spectra in this region likely signals that the transitions here are to spin-orbit states of predominantly triplet origin. In view of the assignment of band V to $E_u(^1E_u)$ of the $(e_u)^3(2a_{1g})$ configuration, the $E_u(^3E_u)$ and $A_{2u}(^3E_u)$ states of this configuration are expected to lower energy right in this region. The $E_u(^3E_u)$ state is predicted from spin-orbit calculations²⁰ to lie lower than $A_{2u}(^3E_u)$. This consideration together with the expected B term signs can be used to assign band III and the positive B term at $3.21 \mu m^{-1}$ to the transition to $E_u(^3E_u)$ and the negative B term at $3.45 \mu m^{-1}$ to the transition to $A_{2u}(^3E_u)$. This latter transition is not resolved in the absorption but may be responsible for the broadness on the low-energy side of band IV. The positive A term expected for the $E_u(^3E_u)$ state is likely obscured by the close proximity of the strong negative B term of band II just to lower energy. Further, the position of the $E_u(^3E_u)$ and $A_{2u}(^3E_u)$ states to 0.6 – $0.8 \mu m^{-1}$ lower energy than the $E_u(^1E_u)$ state (band V) is essentially the same as the 0.6 – $0.7 \mu m^{-1}$ energy difference attributed to $E_u(^1E_u)$ – $E_u(^3E_u)$, $A_{2u}(^3E_u)$ in several mononuclear PtP_4 complexes,¹⁶ which lends credence to the assignments here. The positive B term is not particularly informative although it would be consistent with $E_u(^3B_{1u})$ of $(b_{1u})(2a_{1g})$ if the negative A term for this state were weak or obscured. The $E_u(^3B_{1u})$ state is expected on energetic grounds to lie in this energy region. Other possibilities for band IV such as the $E_u(^3A_{2u})$ state of $(1a_{1g})(2a_{2u})$ or $E_u(^3E_u)$ or $A_{2u}(^3E_u)$ of $(e_g)^3(2a_{2u})$ seem less satisfactory for energetic reasons or the wrong MCD sign expected or both. The $E_u(^3B_{1u})$ assignment for band IV therefore is adopted, but based on the present data alone the case is not overwhelming and perhaps should be regarded as tentative.

The assignments discussed here for $Pt_2(pop)_4^{4-}$ are also included in Table I.

$Pt_2(pop)_4Cl_2^{4-}$ and $Pt_2(pop)_4Br_2^{4-}$. The pattern of the absorption and MCD spectra for the two dihaloplatinum(III) complexes is remarkably similar. A prominent positive A term associated with band II followed by a strong negative B term for band III is observed in each case. Also a higher energy negative MCD band that has the appearance of a negative B term is associated with band IV in each case, but the position of the MCD minimum is slightly higher in energy than the absorption maximum (see Figure 2 and Table 1), which makes a definite term assignment difficult. Finally, a low-energy shoulder (band I) for $Pt_2(pop)_4Cl_2^{4-}$ corresponds to a noticeable broadness on the low-energy side of band II for $Pt_2(pop)_4Br_2^{4-}$. The MCD in this region consists only of a broad positive maximum at $2.46 \mu m^{-1}$ for the dichloro complex and a similar more poorly resolved positive $\Delta\epsilon_M$ for the dibromo complex.

The intense band III has been assigned¹⁴ as the $d\sigma \rightarrow d\sigma^*$ transition to the $A_{2u}(^1A_{2u})$ state of $(1a_{1g})(1a_{2u})$. The B term observed in the MCD is consistent with this assignment. It is interesting that there is only a small red shift in band III from the chloro to the bromo complex (3.50 – $3.23 \mu m^{-1}$), which indicates only a small involvement of the halogen σ orbitals in $1a_{1g}$ and $1a_{2u}$. The positive A term observed for band II is consistent with the $d\pi^* \rightarrow d\sigma^*$ transition to $E_u(^1E_u)$ of $(e_g)^3(1a_{2u})$, which is expected on energetic grounds to be near in energy to the $d\sigma \rightarrow d\sigma^*$ transition. It is also possible that band I contains a contribution from the $E_u(^3A_{2u})$ state of $(1a_{1g})(1a_{2u})$, since it is 0.5 – $0.6 \mu m^{-1}$

- (21) The following parameters were determined from MCD and absorption moments ($D =$ Debye units): $\bar{A}_1 = +0.0368 D^2$; $\bar{D}_0 = 0.0247 D^2$; $\bar{B}_0 = -6.2 \times 10^{-5} D^2/cm^{-1}$; $\bar{v}_0 = 2.208 \mu m^{-1}$; $\bar{A}_1/\bar{D}_0 = +1.49$. Reference 19 should be consulted for the details on the method of moments.
- (22) Parameters: $\bar{A}_1 = +0.0848 D^2$; $\bar{D}_0 = 0.200 D^2$; $\bar{B}_0 = +2.5 \times 10^{-4} D^2/cm^{-1}$; $\bar{v}_0 = 4.096 \mu m^{-1}$; $\bar{A}_1/\bar{D}_0 = +0.424$.

to lower energy than the transition to the $A_{2u}(^1A_{2u})$ state (band III), and the A term expected for this state is also positive. The transition to the predominantly singlet $E_u(^1E_u)$ likely dominates the spectrum, however. Band II also has a low sensitivity to the halogen ($2.88 \mu\text{m}^{-1}$ for Cl^- vs. $2.79 \mu\text{m}^{-1}$ for Br^-), in keeping with the metal-localized transition. The low-energy shoulder on band II (band I) for $\text{Pt}_2(\text{pop})_4\text{Cl}_2^{4-}$ and the broadness on the low-energy side of band II for $\text{Pt}_2(\text{pop})_4\text{Br}_2^{4-}$ are logically assigned as transitions to states of triplet parentage of $(e_g)^3(^1a_{2u})$. The MCD in this region is not very informative, but the $E_u(^3E_u)$ and $A_{2u}(^3E_u)$ states of $(e_g)^3(^1a_{2u})$ are certainly expected below the energy of $E_u(^1E_u)$, band II.

The high-energy band (band IV) is intense, and its position is nearly halogen independent ($4.63 \mu\text{m}^{-1}$ for Cl^- vs. $4.60 \mu\text{m}^{-1}$ for Br^-). This latter feature tends to rule out a halogen-to-metal LMCT and suggests an allowed metal-localized transition within the Pt_2P_8 cluster. Therefore, the possibilities that may be visualized from Figure 3 are transitions to $E_u(^1E_u)$ of $(e_u)^3(2a_{1g})$, $E_u(^1E_u)$ of $(e_g)^3(2a_{2u})$, and $A_{2u}(^1A_{2u})$ of $(1a_{1g})(2a_{2u})$. However, MCD does not really allow a definitive choice among these possibilities because of the difficulty of the term assignment. For example the two $E_u(^1E_u)$ states should each show a positive A term, but none are apparent. A B term would be anticipated for $A_{2u}(^1A_{2u})$ of $(1a_{1g})(2a_{2u})$, but both this state and $E_u(^1E_u)$ of $(e_g)^3(2a_{2u})$ involve the high-energy $\rho\sigma^*$ orbital and might be expected to occur at too high an energy to be observed. It is possible that band IV may be a combination of possibilities, with stronger B terms from several states obscuring weaker A terms. Further analysis is not possible from the present data.

Conclusions. The MCD spectra of bands I and II for $\text{Pt}_2(\text{pop})_4^{4-}$ and bands II and III for $\text{Pt}_2(\text{pop})_4\text{Cl}_2^{4-}$ or $\text{Pt}_2(\text{pop})_4\text{Br}_2^{4-}$ are quite consistent with, and tend to strengthen, the earlier assignments

of the absorption spectra.^{5-7,9,13,14} In addition, the MCD at high energy for $\text{Pt}_2(\text{pop})_4^{4-}$ provides spectroscopic information on which to base an interpretation of the absorption spectra above $3.0 \mu\text{m}^{-1}$. The assignments suggested here differ slightly from those proposed by Azumi et al. from spin-orbit calculations.¹⁷ In particular, band V of $\text{Pt}_2(\text{pop})_4^{4-}$ is assigned here to the transition to $E_u(^1E_u)$ of $(e_u)^3(2a_{1g})$ while the calculations place the $E_u(^3E_u)$ and $A_{2u}(^3E_u)$ of $(e_u)^3(2a_{1g})$ close together (within band widths) in this region. The MCD expected for such a near degenerate situation would be a strong positive *pseudo A* term¹⁹ in contrast to the weak *A* term-strong *B* term combination observed. There is no doubt however that strong spin-orbit interaction is important in the description of any of the states from configuration involving the metal-based orbitals of the Pt_2P_8 cluster. It is interesting the way that the metal-localized spin-orbit states of Pt_2P_8 dominate the electronic structure of both $\text{Pt}_2(\text{pop})_4^{4-}$ and $\text{Pt}_2(\text{pop})_4\text{X}_2^{4-}$. This description can be compared with that of the mononuclear PtP_4 complexes where the lowest energy states originate from $d_{2u}(z)$ configurations and are also spin-orbit states with significant metal-localized character.¹⁶ This comparison leads to a picture of the Pt_2P_8 cluster as an integrated tetragonal unit that behaves like a "thick" mononuclear PtP_4 complex, and when axial ligands are added on oxidation, only a slight perturbation of the internal orbital structure occurs. The same picture emerges from both a molecular structure¹⁵ and reactivity¹¹ viewpoint for $\text{Pt}_2(\text{pop})_4^{4-}$.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. H.I. also acknowledges the Middle East Technical University for a leave of absence.

Registry No. $\text{Pt}_2(\text{pop})_4^{4-}$, 80011-25-2; $\text{Pt}_2(\text{pop})_4\text{Cl}_2^{4-}$, 87355-26-8; $\text{Pt}_2(\text{pop})_4\text{Br}_2^{4-}$, 87374-25-2.

Contribution from the Research Division, U.S. Army Chemical Research and Development Center, Aberdeen Proving Ground, Maryland 21010

Dimerization of Cobalt(II) Tetrasulfonated Phthalocyanine in Water and Aqueous Alcoholic Solutions

YU-CHU YANG,*† J. RICHARD WARD,* and REGINALD P. SEIDERS*

Received August 20, 1984

The dimerization of cobalt(II) tetrasulfonated phthalocyanine (CoTSPC) was studied in water and aqueous alcoholic solutions. The molar absorptivities, ϵ_M and ϵ_D , of the monomer and dimer species at 662 nm and the dimerization constant K_D were calculated from absorbance measurements by modifying a procedure devised by Monahan. The calculated ϵ_M agreed with the measured value of $1.21 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$; both ϵ_D and K_D values were significantly higher than previously published results, which were obtained by successive approximation methods. At a constant temperature, K_D was independent of the total CoTSPC concentration until a limiting concentration was reached. This concentration limit became lower as temperature was reduced and the extent of aggregation increased, implying that higher aggregates than the dimer were present despite the presence of an isosbestic point at 364 nm in a CoTSPC solution as concentrated as $2 \times 10^{-5} \text{ M}$. A finite and positive ΔC_p° of 0.1 kcal/(mol K) was measured over the temperature range 25–75 °C. This precluded "hydrophobic bonding" as a major factor in CoTSPC dimerization. Measurements of dimerization in aqueous methanol, ethanol, and 2-propanol solutions showed that, for a given mole fraction of alcohol, ethanol was more effective than methanol in promoting monomer formation.

Introduction

The past several years have seen increasing interest in the chemistry of the metallophthalocyanines, since these compounds are used as commercial dyes, optical and electrical materials, catalysts, and models for naturally occurring macrocycles.¹ Particular attention has focused on the water-soluble, tetrasulfonate derivative (Figure 1) since Abel and associates² discovered that the cobalt(II) complex binds oxygen reversibly. Abel's work sparked further experiments with oxygenated TSPC complexes³⁻⁷ that led to their use as oxidation catalysts in homogeneous solutions⁸⁻¹³ and on supports.¹⁴⁻²⁰

As with other water-soluble dyestuffs,²¹ transition-metal TSPC complexes aggregate in water, and the formation of the dimer has

- (1) Boucher, L. J. *Coord. Chem. Macrocyclic Compd.* 1979, 4461-4516.
- (2) Abel, E. W.; Pratt, J. M.; Whelan, R. J. *Chem. Soc. D* 1971, 449-450.
- (3) Veprek-Siska, J.; Schwertnerova, E.; Wagnerova, D. M. *Chimia* 1972, 26, 75-76.
- (4) Gruen, L. C.; Blagrove, R. J. *Aust. J. Chem.* 1973, 26, 319-323.
- (5) Wagnerova, D. M.; Schwertnerova, E.; Veprek-Siska, J. *Collect. Czech. Chem. Commun.* 1974.
- (6) Zwart, J.; van Wolput, J. H. M. C. *J. Mol. Catal.* 1979, 5, 51-64.
- (7) Smith, T. D.; Tan, C. H.; Cookson, D. J.; Pilbrow, J. R. *J. Chem. Soc., Dalton Trans.* 1980, 1297-1299.
- (8) Simonov, A. D.; Keier, N. P.; Kundo, N. N.; Mamaeva, E. K.; Glazneva, G. V. *Kinet. Catal.* 1973, 14, 864-868.
- (9) Wagnerova, D. M.; Schwertnerova, E.; Veprek-Siska, J. *Collect. Czech. Chem. Commun.* 1973, 756-764.

* NRC Senior Research Associate