

**Figure 10.** Dependence of the formation rate of products in the reduction of  $\text{HOCH}_2\text{CH}_2\text{N}_3$  at  $-1.25$  V vs. SCE on the amount of  $(n\text{-Bu}_4\text{N})_3[\text{Mo-Fe}]$  modified on a glassy-carbon electrode in an aqueous  $\text{H}_3\text{PO}_4/\text{NaOH}$  buffer ( $0.2$  mol  $\text{dm}^{-3}$ ) solution (pH 10) containing  $\text{HOCH}_2\text{C-H}_2\text{N}_3$  ( $5.0 \times 10^{-3}$  mol  $\text{dm}^{-3}$ ).

therefore, increases with increasing pH value up to pH 12, where the cluster may be stable.

The reduction of  $\text{HOCH}_2\text{CH}_2\text{N}_3$  ( $5.0 \times 10^{-3}$  mol  $\text{dm}^{-3}$ ) even with  $[\text{Mo-Fe}]/\text{GC}$  in the presence of allyl alcohol ( $0.1$  mol  $\text{dm}^{-3}$ )

in water under electrolysis at  $-1.25$  V (vs. SCE) produces  $\text{N}_2$  and  $\text{HOCH}_2\text{CH}_2\text{NH}_2$  together with  $\text{H}_2$ , and neither  $\text{NH}_3$  nor  $\text{N}_2\text{H}_4$  has been formed at all, suggesting that  $\text{N}_2\text{H}_2$  is involved as a reaction intermediate for the formation of  $\text{N}_2\text{H}_4$  and  $\text{NH}_3$  in the reduction of  $\text{HOCH}_2\text{CH}_2\text{N}_3$  by  $[\text{Mo-Fe}]/\text{GC}$ .

The reduction of  $\text{HOCH}_2\text{CH}_2\text{N}_3$  with  $[\text{Mo-Fe}]/\text{GC}$  under electrolysis at  $-1.10$  V (vs. SCE) gave only  $\text{HOCH}_2\text{CH}_2\text{NH}_2$  and  $\text{N}_2$  without forming either  $\text{NH}_3$ ,  $\text{N}_2\text{H}_4$ , or  $\text{H}_2$ . Thus, the anodic shift of the electrode potential from  $-1.25$  to  $-1.10$  V vs. SCE resulted in a decrease of the ability of the multielectron reduction of  $[\text{Mo-Fe}]/\text{GC}$ . Such a characteristic behavior of  $[\text{Mo-Fe}]/\text{GC}$  toward the reduction of alkyl azide can be explained from the cathodic polarization curves of the electrode (Figure 4); the limiting currents of  $[\text{Mo-Fe}]/\text{GC}$  observed between  $-1.0$  and  $-1.1$  V (vs. SCE) in the presence  $\text{HOCH}_2\text{CH}_2\text{N}_3$  are, therefore, due to the two-electron reduction of  $\text{HOCH}_2\text{CH}_2\text{N}_3$  and an increase of the current at more negative than  $-1.10$  V (vs. SCE) results from the multielectron reduction of  $\text{HOCH}_2\text{CH}_2\text{N}_3$  accompanied by  $\text{H}_2$  evolution.

**Registry No.**  $(\text{Bu}_4\text{N})_3[\text{Mo-Fe}]$ , 68197-68-2;  $(\text{Et}_4\text{N})_3[\text{Mo-Fe-OH}]$ , 79466-71-0;  $[\text{Mo-Fe}]^{3-}$ , 68136-29-8;  $[\text{Mo-Fe}]^{4-}$ , 81276-61-1;  $[\text{Mo-Fe}]^{5-}$ , 76125-83-2;  $\text{CH}_3\text{N}_3$ , 624-90-8;  $\text{HOCH}_2\text{CH}_2\text{N}_3$ , 1517-05-1;  $\text{H}_2$ , 1333-74-0;  $\text{N}_2$ , 7727-37-9;  $\text{NH}_3$ , 7664-41-7;  $\text{N}_2\text{H}_4$ , 1333-74-0;  $\text{CH}_3\text{NH}_2$ , 74-89-5;  $\text{HOCH}_2\text{CH}_2\text{NH}_2$ , 141-43-5; carbon, 7440-44-0; allyl alcohol, 107-18-6.

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## Electronic Absorption and Magnetic Circular Dichroism Spectra of Monomeric and Dimeric Platinum(II) and Palladium(II) Iodide Complexes

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Magnetic circular dichroism (MCD) and absorption spectra of  $\text{PdI}_4^{2-}(\text{aq})$  for  $1/\lambda < 3.8$   $\mu\text{m}^{-1}$  and of  $\text{PtI}_4^{2-}$  and  $\text{Pt}_2\text{I}_6^{2-}$  for  $1/\lambda < 5.0$   $\mu\text{m}^{-1}$  in methanol and at  $-65$   $^\circ\text{C}$  have been recorded. In the latter complexes, there is intense absorption ( $\epsilon = 5 \times 10^4$   $\text{cm}^{-1} \text{M}^{-1}$ ) in the UV region and several bands have been detected. The well-established LMCT (ligand p to metal d) assignment for  $\text{PdX}_4^{2-}$  holds also for  $\text{PdI}_4^{2-}$  with singlet-triplet transitions included. The most plausible assignment for  $\text{PtI}_4^{2-}$  seems to be a combination of LMCT and internal metal d-p transitions. The vis/near-UV bands have been assigned as singlet-triplet transitions, the far-UV bands as the corresponding singlet-singlet d-p transitions, and the bands between these systems as LMCT transitions.

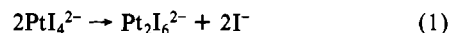
### Introduction

For many years the electronic structures as revealed by the spectra and spectral assignments of square-planar ( $D_{4h}$ )  $d^8$  complexes of platinum(II) and palladium(II) have attracted much attention. The first attempts<sup>1</sup> concentrated on the symmetry-forbidden d-d (ligand field) bands in  $\text{PtCl}_4^{2-}$ . The assignments were established from single-crystal<sup>2</sup> and magnetic circular dichroism (MCD) spectra.<sup>2,3</sup> When such measurements were extended to the symmetry-allowed bands in the UV region,<sup>3,4</sup> the results showed that different assignments must be given for  $\text{PtCl}_4^{2-}$  and  $\text{PdCl}_4^{2-}$ . The two suggestions were ligand-to-metal charge transfer (LMCT) for the bands in  $\text{PdCl}_4^{2-}$  but metal d to metal p charge transfer for at least one band in  $\text{PtCl}_4^{2-}$  (this was first suggested by Chatt et al.<sup>1</sup> in their early study). That internal metal transitions (i.e. d to p) should occur at considerably lower energies in Pt as compared to Pd could be inferred from both atomic spectral data<sup>4</sup> and MO calculations.<sup>5</sup>

Unfortunately, the assignments for the chloride complexes are based on two high-intensity bands<sup>6</sup> only. There are only those two bands below the high-energy limit of commercial spectro-

photometers ( $5.3$   $\mu\text{m}^{-1}$  or  $185$  nm). A possible way to increase the number of bands would be to substitute chloride by bromide<sup>7</sup> and iodide: the concomitant red shift would make more bands accessible. Thus, for  $\text{PtBr}_4^{2-}$  Isci and Mason<sup>7</sup> found additional strong bands in the UV region that they assigned to a mixture of internal metal and LMCT transitions.

This work presents a similar study of  $\text{PtI}_4^{2-}$  and  $\text{PdI}_4^{2-}$ . These complexes are only stable in solutions containing a large excess of ligand<sup>8,9</sup> ( $C_1 \geq 0.5$  M); otherwise, disturbing reactions take place within a few seconds: solvolysis and precipitation take place in water ( $\text{PtI}_2$ ,  $\text{PdI}_2$ ) and formation of the dimer occurs especially in organic solvents ( $\text{Pt}_2\text{I}_6^{2-}$  and its Pd analogue)



Unfortunately,  $\text{I}^-$  has a very strong absorption in the UV region,<sup>9</sup> which prevents measurements above  $3.8$   $\mu\text{m}^{-1}$  ( $260$  nm). However, by a low-temperature technique, described elsewhere,<sup>10</sup> it has been possible to keep  $\text{PtI}_4^{2-}$  in solution without added  $\text{I}^-$  for the time needed to record its absorption and MCD spectra to  $5.0$   $\mu\text{m}^{-1}$  (cf. Figure 3).

As expected, the spectra of the iodide complexes contain many more symmetry-allowed bands than those of the chloride complexes. This is not only due to the expected red shift; in the iodide

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**Table I.** Spectrophotometric Room-Temperature Equilibrium Measurements and Equilibrium Constant Calculated according to Eq 1

$C_1/\text{mM}$	$\text{H}_2\text{O}$				$\text{CH}_3\text{OH}$		
	$1/\lambda = 3.02 \mu\text{m}^{-1}$		$1/\lambda = 3.30 \mu\text{m}^{-1}$		$1/\lambda = 2.99 \mu\text{m}^{-1}$		
	$\epsilon/\text{cm}^{-1}$	$K_1/\text{M}$	$\epsilon/\text{cm}^{-1}$	$K_1/\text{M}$	$C_1/\text{mM}$	$\epsilon/\text{cm}^{-1}$	$10^{-3}K_1/\text{M}$
25.0	2.18	10.8	2.50	10.4	120	0.173	2.0
45.0	2.59	9.2	2.02	7.9	160	0.190	2.1
75.0	3.08	7.9	1.51	7.0	200	0.203	2.2
105	3.38	7.8	1.17	6.7	300	0.247	1.8
145	3.65	7.8	0.890	6.4	500	0.296	1.7
245	3.95	8.3	0.600	6.6			
505	4.13	11.7	0.460	11.5			
		av $9.1 \pm 1.6$		av $8.1 \pm 2.0$			av 2

complexes the LMCT bands of singlet-triplet origin may be considerably stronger than those in the chloride complexes. The existence of such transitions in  $\text{PdBr}_4^{2-}$  have been suggested by Martin et al.<sup>11</sup> to account for the shoulders at the low-energy sides of the singlet-singlet transitions (cf. ref 6, Figure 7). As is well-known, the "allowedness" of singlet-triplet transitions is explained by the presence of the spin-orbit interaction,<sup>12</sup> which increases with atomic number (i.e.  $\text{Cl}^- < \text{Br}^- < \text{I}^-$ ). It also gives rise to a splitting of the triplet states. For internal metal transitions (d-d, d-p) the effect is evidently larger for Pt than for Pd. This is clearly revealed by the spectra of the assigned singlet-triplet transitions among the d-d bands, which have lower intensities in Pd as compared to those in Pt (cf. ref 11, p 2546). As discussed by Martin et al.,<sup>13</sup> it is possible to make a thorough analysis of the d-d spectrum of  $\text{PtCl}_4^{2-}$  only if the spin-orbit effect is taken into account. Obviously, it is necessary to consider it also in the assignments of the internal metal transitions of the d-to-p type.

A deeper knowledge of the electronic structure can often be achieved if spectra of complexes with the same central atom but slightly different symmetries are compared.<sup>6</sup> In this case the symmetry can be varied in a highly specific way: the existence of a dimer ( $\text{Pt}_2\text{I}_6^{2-}$ ) means that additional information can be obtained from a complex composed of identical atoms in the same oxidation states and with the geometrical arrangement around each metal atom nearly identical with that in the monomer. Absorption spectra of the monomer and dimer are thus expected to be only slightly different.<sup>14</sup> It is obviously essential to know about the equilibrium according to eq 1. The equilibrium constant ( $K_1/\text{M}$ ) is reported here. A study of the corresponding Pd reaction has been published.<sup>9</sup>

Very little has been published<sup>8,15</sup> about the synthesis and structure of salts containing the  $\text{PtI}_4^{2-}$  and  $\text{PdI}_4^{2-}$  ions. Both are expected to be isostructural with the corresponding chloride complexes, i.e. square planar. The magnetic property of the ground state (diamagnetic) and the features of the MCD spectra reported here are in agreement with this assumption. The corresponding dimers are assumed to be isostructural with  $\text{Pt}_2\text{Br}_6^{2-}$  (i.e.  $D_{2h}$ ; cf. ref 16). An estimate of the Pt-I distances has been published.<sup>17</sup>

### Experimental Section

**Chemicals and Solutions.** Methanol (Merck Uvasol), doubly distilled water, and 5 M aqueous sulfuric acid (fp  $-75^\circ\text{C}$ ), prepared from  $\text{H}_2\text{SO}_4$  (Merck p.a. 98%) flushed with nitrogen, were used. Potassium tetraiodoplatinate(II) dihydrate  $\text{K}_2\text{PtI}_4 \cdot 2\text{H}_2\text{O}$  was synthesized from  $\text{K}_2\text{PtCl}_4$  (Johnson Matthey) and potassium iodide (Merck p.a.) in water and under inert atmosphere (this prevents oxidation of platinum(II) to platinum(IV) by triiodide, with the latter formed from the air oxidation of iodide). A 1.0-g sample of  $\text{K}_2\text{PtCl}_4$  was dissolved in 5.0 mL of water,

and 4.0 mL of saturated KI(aq) was added. After 15 h, 50 mL of acetone (Merck p.a.) was added. KCl precipitated, and the solution was decanted to a beaker. The precipitate was washed with  $4 \times 25$  mL of acetone (Merck p.a.), which was decanted between each portion. Acetone was removed by flushing with nitrogen. The beaker and a drying agent were placed in a nitrogen-filled desiccator. After about 2 days, a small volume (e.g. 1 mL) was left and a dark fine crystalline precipitate was formed. The water was decanted off and the precipitate dried. Besides the platinum product, it contained also transparent crystals of KI. These were removed mechanically. Anal. Calcd for  $\text{K}_2\text{PtI}_4 \cdot 2\text{H}_2\text{O}$ : K, 9.6; I, 62.1; Pt 23.9. Found: K, 9.84; I, 65.0; Pt, 23.5.

**Apparatus and Measurements.** Electronic absorption and MCD spectra were recorded on a Varian Cary 2290 spectrophotometer and a JASCO J-41A polarimeter, respectively. The latter was equipped with a permanent magnet described elsewhere.<sup>18</sup> The magnetic field strength was 1.0 T in a 4-mm air gap, and the optical path length was 1.00 mm. Spectral measurements on  $\text{PdI}_4^{2-}$  were performed at room temperature by the dissolution of  $\text{K}_2\text{PdCl}_4$  in 1 M KI(aq) so that  $C_{\text{Pd}} \approx 8 \times 10^{-4}$  M. With these concentrations,  $\text{Pd}_2\text{I}_6^{2-}$  can be neglected.<sup>9</sup> Because of the high UV absorption of iodide, the accessible spectral region is limited to  $<3.8 \mu\text{m}^{-1}$ . For  $\text{PtI}_4^{2-}$  free iodide can be excluded by performing the measurements in methanol and at  $-65^\circ\text{C}$  ( $1/\lambda \leq 5.1 \mu\text{m}^{-1}$ ). A check showed that the Lambert-Beer law holds to within 10% even at  $1/\lambda = 5.1 \mu\text{m}^{-1}$ . The low transmittance of methanol in the UV region prevents absorption measurements above  $5.1 \mu\text{m}^{-1}$  and MCD measurements above  $4.7 \mu\text{m}^{-1}$ . At the low temperature used the measured solutions were stored in a closed-flow, thermostatable vessel<sup>10,19</sup> connected to a flow-through cell (Hellma 170-QS, optical path lengths 10.00 or 2.00 mm and 1.00 mm (MCD)). The vessel contained 100 mL of nitrogen-flushed methanol. A small amount (e.g. 10 mg) of finely divided  $\text{K}_2\text{PtI}_4 \cdot 2\text{H}_2\text{O}$  was stored in the weighing scoop,<sup>19</sup> which was fed by a slow stream of dry nitrogen. The temperature was decreased to  $-65 (\pm 1)^\circ\text{C}$  and a base line recorded between 2 and  $5 \mu\text{m}^{-1}$ .  $\text{K}_2\text{PtI}_4 \cdot 2\text{H}_2\text{O}$  was added by opening the weighing scoop and increasing the nitrogen stream through it. The complex dissolved within 2 min, and about 1 min later a constant absorbance value was reached (measured at an absorption maximum). A scan was performed between 2.5 and  $5.0 \mu\text{m}^{-1}$ . The lower limit was set to check that the spectrum was in agreement with that of  $\text{PtI}_4^{2-}$  (and not  $\text{Pt}_2\text{I}_6^{2-}$ ) for  $1/\lambda < 3.3 \mu\text{m}^{-1}$  (cf. Figure 1c). The spectrum changed only a few percent within 10 min. The temperature of the solution was then allowed to increase. By this the rate of formation of  $\text{Pt}_2\text{I}_6^{2-}$  (cf. eq 1) was enhanced. When all the  $\text{PtI}_4^{2-}$  had been converted, the temperature was decreased ( $-65^\circ\text{C}$ ) and a spectrum of  $\text{Pt}_2\text{I}_6^{2-}$  (and  $\text{I}^-$ ; cf. eq 1) was obtained. A separately recorded spectrum of  $\text{I}^-$  ( $\text{KI}(\text{CH}_3\text{OH})$ ,  $t = -65^\circ\text{C}$ ) was measured and subtracted. The largest (about 30%) contribution from  $\text{I}^-$  comes at  $4.60 \mu\text{m}^{-1}$  ( $\epsilon_1 = 1.7 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$ ).

A spectrum of  $\text{PtI}_4^{2-}$  in 5 M  $\text{H}_2\text{SO}_4$ (aq), at  $-50^\circ\text{C}$ , and for  $3.4 < 1/\lambda < 4.2 \mu\text{m}^{-1}$  was also recorded (cf. Figure 3b). In this medium the resolution was slightly better than in  $\text{CH}_3\text{OH}$ , but the precipitation of  $\text{PtI}_2$ (s) was disturbing (this reaction is absent in  $\text{CH}_3\text{OH}$ ). (Even in this case it was checked that the spectrum agreed with that of  $\text{PtI}_4^{2-}$ (aq) for  $1/\lambda < 3.3 \mu\text{m}^{-1}$ ).

The equilibrium according to eq 1 was spectrophotometrically studied in water and methanol at room temperature. The concentrations are displayed in Table I and Figure 1.

Magnetic susceptibilities were measured with a Faraday balance described elsewhere.<sup>20</sup> The sample consisted of about 25 mg of polycrystalline material, measured at two field strengths (0.3 and 0.4 T) and between  $-195$  and  $+50^\circ\text{C}$  in steps of  $3^\circ\text{C}$ .

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Table II. Spectral Data for PdI<sub>4</sub><sup>2-</sup><sup>a</sup>

band	(1/λ) <sub>max</sub> /μm <sup>-1</sup>	σ/μm <sup>-1</sup>	10 <sup>-3</sup> ε <sub>max</sub> /cm <sup>-1</sup> M <sup>-1</sup>	f	D/D <sup>2</sup>	MCD A term/ D <sup>2</sup> μ <sub>B</sub>	assignments
I	1.84	0.13	2.77	0.033	3.8		<sup>3</sup> E <sub>u</sub> , <sup>3</sup> A <sub>2u</sub> 3b <sub>1g</sub> (d <sub>x<sup>2</sup>-y<sup>2</sup>) ← 1b<sub>2u</sub>, 3e<sub>u</sub> (ligand pπ)</sub>
II	2.07	0.13	4.05	0.049	5.0		
III	2.45	0.14	11.0	0.14	12		<sup>1</sup> E <sub>u</sub> , <sup>1</sup> A <sub>2u</sub> 3b <sub>1g</sub> (d <sub>x<sup>2</sup>-y<sup>2</sup>) ← 1b<sub>2u</sub>, 3e<sub>u</sub> (ligand pπ)</sub>
IV	3.17	0.19	16.7	0.29	20	12	<sup>3</sup> E <sub>u</sub> 3b <sub>1g</sub> (d <sub>x<sup>2</sup>-y<sup>2</sup>) ← 2e<sub>u</sub> (ligand pσ)</sub>
V	3.74	0.18	22	0.37	21	17	<sup>1</sup> E <sub>u</sub> 3b <sub>1g</sub> (d <sub>x<sup>2</sup>-y<sup>2</sup>) ← 2e<sub>u</sub> (ligand pσ)</sub>

<sup>a</sup>Medium: 1.0 M KI(aq) (room temperature).

Table III. Spectral Data for PtI<sub>4</sub><sup>2-</sup><sup>a</sup>

band	(1/λ) <sub>max</sub> /μm <sup>-1</sup>	σ/μm <sup>-1</sup>	10 <sup>-3</sup> ε <sub>max</sub> /cm <sup>-1</sup> M <sup>-1</sup>	f	D/D <sup>2</sup>	MCD A term/ D <sup>2</sup> μ <sub>B</sub>	suggested assigns (orbitals only)
I	2.26	0.15	1.28	0.018	1.7		singlet-triplet: 2a <sub>2u</sub> (metal p) ← 2e <sub>g</sub> , 3a <sub>1g</sub> (metal d)
II	2.54	0.11	4.47	0.045	3.8	-0.5	
III	2.96	0.14	6.76	0.087	6.3		
IV	3.63	0.21	3.41	0.066	3.9		LMCT, singlet-singlet, and singlet-triplet: 3b <sub>1g</sub> (d <sub>x<sup>2</sup>-y<sup>2</sup>) ← 1b<sub>2u</sub>, 3e<sub>u</sub>, 2e<sub>u</sub></sub>
V	3.76	0.14	7.90	0.10	5.8		
VI	4.01	0.15	13.7	0.19	10	1	singlet-singlet: 2a <sub>2u</sub> (metal p) ← 2e <sub>g</sub> , 3a <sub>1g</sub> (metal d) and CTTS (see text)
VII	4.38	0.20	46.5	0.86	42	26	
VIII	4.74	0.17	33.2	0.52	23		
IX	5.02	0.16	25.9	0.38	16		

<sup>a</sup>Media: CH<sub>3</sub>OH (t = -65 °C, bands I-III and VII-IX); 5 M H<sub>2</sub>SO<sub>4</sub>(aq) (t = -50 °C, bands IV-VI)

## Results

**Equilibrium Measurements.** Parts a and b of Figure 1 display the absorbance changes for constant (excess) C<sub>I</sub> and varying C<sub>Pt</sub> (C<sub>I</sub>/C<sub>Pt</sub> > 70) and constant C<sub>Pt</sub> and varying C<sub>I</sub> (C<sub>I</sub>/C<sub>Pt</sub> > 50), respectively (cf. Table I). Obviously, only two absorbing species exist (isosbestic points) and the shape of the spectra in Figure 1a are so similar to those in Figure 1b that the two species must be the same in both series of measurements. The changes in Figure 1a demonstrate clearly that a polynuclear complex must be present, since any equilibrium quotient between two mononuclear complexes remains constant, i.e. independent of C<sub>Pt</sub> as long as [I<sup>-</sup>] is constant. The only reported polynuclear complex of iodo-platinate(II) is the dimer Pt<sub>2</sub>I<sub>6</sub><sup>2-</sup>; cf. ref 8. When C<sub>Pt</sub> decreases (spectrum 4 in Figure 1a), Pt<sub>2</sub>I<sub>6</sub><sup>2-</sup> is converted to a monomer. That this one is PtI<sub>4</sub><sup>2-</sup> is consistent with the fact that the absorbance changes for decreasing C<sub>Pt</sub> (Figure 1a) are the same as those for increasing C<sub>I</sub> (Figure 1b). The validity of the equilibrium according to eq 1 is quantitatively demonstrated by the constancy of the concentration ratio

$$K_1 = [\text{PtI}_6^{2-}][\text{I}^-]^2 / [\text{PtI}_4^{2-}]^2 \quad (2)$$

displayed in Table I. The concentrations either are known ([I<sup>-</sup>] = C<sub>I</sub>) or can be calculated from the known total concentration of Pt and the absorbance

$$C_{\text{Pt}} = [\text{PtI}_4^{2-}] + 2[\text{Pt}_2\text{I}_6^{2-}] \quad (3)$$

$$e = \epsilon_4[\text{PtI}_4^{2-}] + \epsilon_{26}[\text{Pt}_2\text{I}_6^{2-}] \quad (4)$$

where *e* is the absorptivity (cm<sup>-1</sup>) and  $\epsilon$  the molar absorptivity (M<sup>-1</sup> cm<sup>-1</sup>).  $\epsilon_{26}$  can be calculated from a plot of *e* vs. C<sub>I</sub> by extrapolating to C<sub>I</sub> = 0 (cf. Figure 1b), and  $\epsilon_4$ , from a separately recorded spectrum of a dilute solution of K<sub>2</sub>PtCl<sub>4</sub> (C<sub>Pt</sub> ≈ 1 × 10<sup>-4</sup> M) in 1 M KI(aq). K<sub>1</sub> was calculated from absorbance values at 3.02 μm<sup>-1</sup> ( $\epsilon_4 = 8.3 (1) \times 10^3$ ,  $\epsilon_{26} = 6.4 (1) \times 10^3$  M<sup>-1</sup> cm<sup>-1</sup>) and 3.30 μm<sup>-1</sup> ( $\epsilon_4 = 9.0 (3) \times 10^2$ ,  $\epsilon_{26} = 1.3 (1) \times 10^4$  M<sup>-1</sup> cm<sup>-1</sup>); cf. Table I. The two values agree satisfactorily. The mean value of K<sub>1</sub> and its estimated error is K<sub>1</sub> = 9 ± 3 M. From this value the spectra of PtI<sub>4</sub><sup>2-</sup> and Pt<sub>2</sub>I<sub>6</sub><sup>2-</sup> displayed in Figure 1c have been calculated. The spectrum of PtI<sub>4</sub><sup>2-</sup>(aq) for 1/λ < 3.4 μm<sup>-1</sup> consists of two maxima and a pronounced minimum in the near-UV region. It agrees satisfactorily with that published by Corain and Poë.<sup>8</sup> The spectrum of K<sub>2</sub>PtI<sub>4</sub>·2H<sub>2</sub>O dissolved in methanol at -65 °C (Figure 3a) is obviously only compatible with PtI<sub>4</sub><sup>2-</sup>.

**Magnetic Susceptibility.** From a plot of the inverse of the magnetic susceptibility vs. absolute temperature it can be concluded that the compound is diamagnetic: the susceptibility is

Table IV. Spectral Data for Pt<sub>2</sub>I<sub>6</sub><sup>2-</sup><sup>a</sup>

band	(1/λ) <sub>max</sub> /μm <sup>-1</sup>	σ/μm <sup>-1</sup>	10 <sup>-3</sup> ε <sub>max</sub> /cm <sup>-1</sup> M <sup>-1</sup>	f	D/D <sup>2</sup>
I	2.22	0.15	2.23	0.025	3.0
II	2.53	0.16	7.99	0.12	9.9
III	2.87	0.15	4.44	0.061	4.6
IV	3.23	0.18	8.24	0.14	9.0
V	3.59	0.17	33.8	0.53	31
VI	4.16	0.21	36.7	0.71	36
VII	4.57	0.17	54.1	0.85	39
VIII	4.84	0.16	41.4	0.61	27
IX	5.06	0.14	41.2	0.53	22

<sup>a</sup>Medium: CH<sub>3</sub>OH (t = -65 °C).

slightly negative and temperature-independent.

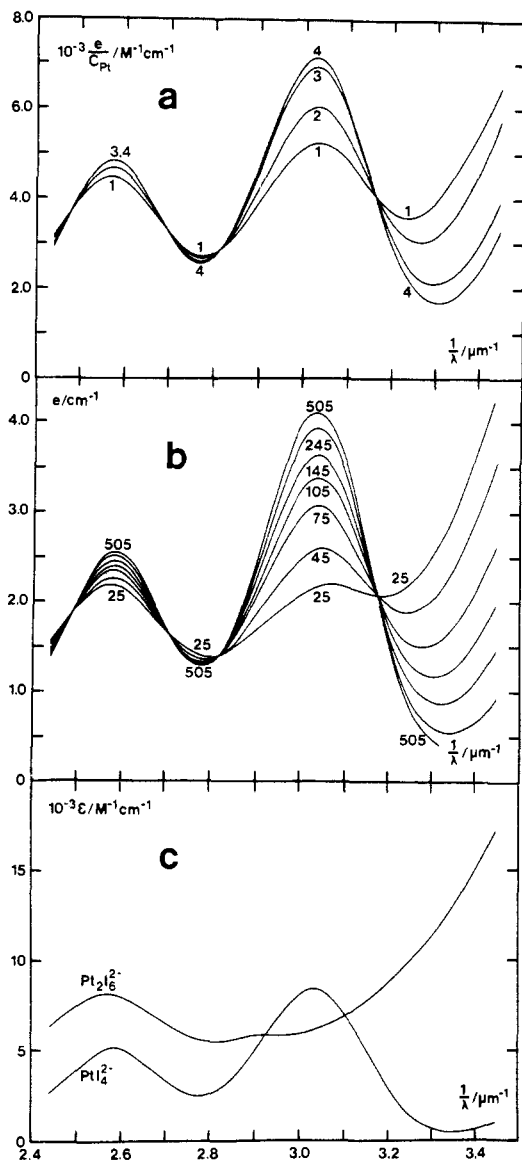
**Spectral Data.** The absorption and MCD spectra are displayed in Figures 2-4. Least-squares calculations assuming Gaussian band shapes<sup>21</sup> have been performed on the absorption data (ε vs. 1/λ). The parameters obtained are collected in Tables II-IV. The MCD A terms have been estimated from the equations given in ref 21 (with *d<sub>j</sub>* replaced by σ<sub>j</sub>/(ln 2)<sup>1/2</sup>, where 2σ<sub>j</sub> is the bandwidth for band *j* at half-height intensity). In these, the largest deflection of Δε is inserted. For B terms this occurs at (1/λ)<sub>max</sub> and for A terms, at 1/λ = (1/λ)<sub>max</sub> ± σ/(2 ln 2)<sup>1/2</sup> with (1/λ)<sub>max</sub> and σ taken from the least-squares calculations on the absorption data. The sign convention adopted by Stephens<sup>22</sup> has been used (the sign of the B term is reversed as compared to its sign given by eq 4 of ref 21).

The spectrum of PdI<sub>4</sub><sup>2-</sup>, displayed in Figure 2, shows well-separated bands, which make the analysis simple and reliable. However, the UV spectrum of PtI<sub>4</sub><sup>2-</sup> shows regions of broad absorption that make the analysis uncertain, especially as to the number of bands. At 3.4 < 1/λ < 3.9 μm<sup>-1</sup> the fit with only one band is poor for PtI<sub>4</sub><sup>2-</sup> (CH<sub>3</sub>OH), with deviations between calculated and observed values up to 13% despite the rather high molar absorptivities. The spectrum in 5 M H<sub>2</sub>SO<sub>4</sub>(aq) (cf. Figure 3b) reveals that there are at least two bands. However, even if a least-squares calculation (data from 5 M H<sub>2</sub>SO<sub>4</sub>(aq)) with two bands gives a better fit (maximum deviation 6%), the bandwidths will be large: σ = 0.23 μm<sup>-1</sup> for both bands ((1/λ)<sub>max</sub> = 4.01 and

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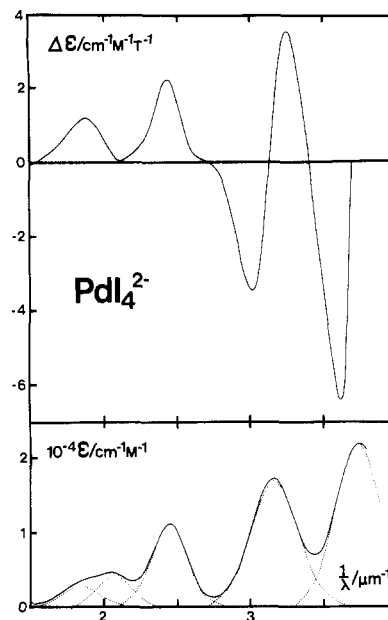
(23) Nakayama, K.; Komorita, T.; Shimura, Y. *Bull. Chem. Soc. Jpn.* 1984, 57, 972.



**Figure 1.** Spectrophotometric equilibrium measurements according to eq 1: (a) constant  $C_1$  (75 mM) and varying platinum concentrations,  $10^4 C_{Pt}$  = (1) 10.3, (2) 5.13, (3) 1.28, and (4) 0.513 M; (b) constant  $C_{Pt}$  ( $5.13 \times 10^{-4}$  M) with varying  $C_1$  (in mM) indicated (cf. Table I). Calculated spectra of  $PtI_4^{2-}$  and  $Pt_2I_6^{2-}$  in water and at room temperature are shown in part c.

$3.77 \mu\text{m}^{-1}$ ). With three bands (as indicated in Figure 3b), the fit is excellent and the bandwidths are reduced to the values given in Table III. It should be remarked that the  $(1/\lambda)_{\text{max}}$  values for the two stronger bands coincide with those calculated under the assumption of two bands only (i.e.  $4.01$  and  $3.76 \mu\text{m}^{-1}$ ; cf. Table III).

The MCD spectrum in this region (cf. Figure 3b) is obviously in conformity with (at least) two bands. A possible interpretation would be that the band at higher energy ( $4.01 \mu\text{m}^{-1}$ , 5 M  $\text{H}_2\text{SO}_4(\text{aq})$ ) is connected with a positive  $A$  term, the negative lobe of which is seen in 5 M  $\text{H}_2\text{SO}_4(\text{aq})$  and the positive lobe of which is seen in  $\text{CH}_3\text{OH}$ . This explains that  $\Delta\epsilon = 0$  close to the maximum of the Gaussian band ( $4.01 \mu\text{m}^{-1}$ ) in 5 M  $\text{H}_2\text{SO}_4(\text{aq})$ . Moreover, with the bandwidth obtained by assuming three bands (i.e.  $\sigma = 0.15 \mu\text{m}^{-1}$ ,  $(1/\lambda)_{\text{max}} = 4.01 \mu\text{m}^{-1}$ ; cf. Table III) the position of maximum deflection (in  $\Delta\epsilon$ ) for an  $A$  term would come at  $3.88 \mu\text{m}^{-1}$ , which is close to the experimental value ( $3.91 \mu\text{m}^{-1}$ ; cf. Figure 3b). With the higher bandwidth obtained with two bands (i.e.  $\sigma = 0.23 \mu\text{m}^{-1}$ ,  $(1/\lambda)_{\text{max}} = 4.01 \mu\text{m}^{-1}$ ) this position would be  $3.81 \mu\text{m}^{-1}$ . However, as seen in Figure 3b,  $\Delta\epsilon$  is here close to zero. To conclude, it seems consistent to assume three bands and to connect the MCD features around the band max-



**Figure 2.** MCD and absorption spectra of  $PdI_4^{2-}(\text{aq})$ . Dotted lines indicate the Gaussian bands.

imum at  $4.01 \mu\text{m}^{-1}$  with a positive  $A$  term. (With the same reasoning it is also possible to connect the band at  $3.77 \mu\text{m}^{-1}$  with a negative  $A$  term, but then it is hard to explain the presence of the positive  $\Delta\epsilon$  values in  $\text{CH}_3\text{OH}$  around  $3.75 \mu\text{m}^{-1}$ . These can only be due to a positive  $A$  term or to a  $B$  term).

Concerning the MCD spectrum at lower energies ( $1/\lambda < 3.8 \mu\text{m}^{-1}$ , 5 M  $\text{H}_2\text{SO}_4(\text{aq})$ ; cf. Figure 3b) with  $\Delta\epsilon < 0$ , it is reasonable to assume a negative  $B$  term connected with the band at  $3.62 \mu\text{m}^{-1}$ . Due to the presence of two strongly overlapping absorption bands ( $3.62$  and  $3.77 \mu\text{m}^{-1}$ ; Cf. Table III), other alternatives can obviously not be excluded.

In the broad absorption for  $1/\lambda > 4 \mu\text{m}^{-1}$  (cf. Figure 3a) it is possible to get an acceptable fit with only two bands (maximum deviation  $\leq 3\%$ ). However, the band with lower energy ( $4.4 \mu\text{m}^{-1}$ ) will then have a smaller  $\epsilon_{\text{max}}$  than the band at  $4.8 \mu\text{m}^{-1}$ . For this band the bandwidth will be unusually large,  $2\sigma \approx 0.6 \mu\text{m}^{-1}$ . With three bands, the fit is of course better, and the more plausible results for  $\epsilon_{\text{max}}$  and  $\sigma$  displayed in Table III and Figure 3a are obtained. Concerning the MCD terms for these bands, the one at  $4.38 \mu\text{m}^{-1}$  can with certainty be connected with a positive  $A$  term for the following reasons: the band shape is in agreement with such a term and the position of largest deflection (at  $4.20 \mu\text{m}^{-1}$ , where  $\Delta\epsilon = -9.7 \mu\text{m}^{-1} \text{M}^{-1} \text{T}^{-1}$ ; cf. Figure 3a) coincides with the value calculated from absorption data (cf. Table III; at  $4.20 \mu\text{m}^{-1}$  the influences from the surrounding bands at  $4.74$  and  $3.80 \mu\text{m}^{-1}$  can be neglected, because the difference is larger than  $3\sigma$  and  $\epsilon_{\text{max}}$  is too low ( $3.80 \mu\text{m}^{-1}$ ). The highest positive deflection should then come at  $4.56 \mu\text{m}^{-1}$ . The experimental value is here about  $2 \text{cm}^{-1} \text{M}^{-1} \text{T}^{-1}$ , which implies that there must be a large negative contribution (about  $-7 \text{M}^{-1} \text{cm}^{-1} \text{T}^{-1}$ ) from the band at  $4.74 \mu\text{m}^{-1}$  (the contribution from the band at  $5.02 \mu\text{m}^{-1}$  can be neglected here). Whether this comes from a positive  $A$  and/or a negative  $B$  term (both connected with the band at  $4.74 \mu\text{m}^{-1}$ ) can hardly be determined from the present data, partly because the contribution at higher energies from the band at  $5.02 \mu\text{m}^{-1}$  is completely unknown.

## Discussion

**Ground-State Properties.** The diamagnetism exhibited by  $PtI_4^{2-}$  shows that the ground state is best described by a nondegenerate, singlet term ( $^1A_{1g}$ ,  $D_{4h}$ ). This fact, together with the MCD  $A$  terms (cf. Figures 2 and 3), indicates that the assumed symmetry ( $D_{4h}$ ) is probable.

**Assignments.** The spectral data are displayed in Tables II–IV and Figures 2–4. Data for  $PdCl_4^{2-}(\text{aq})$ ,  $PdBr_4^{2-}(\text{aq})$ , and  $PdI_4^{2-}(\text{aq})$  are collected in Figure 5.

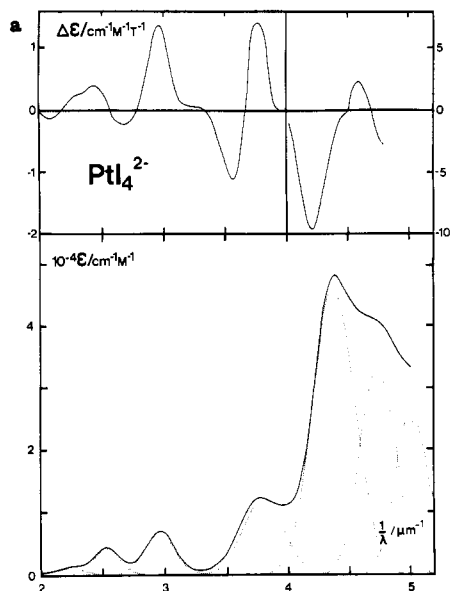
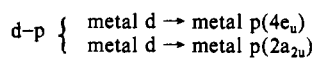


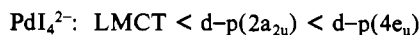
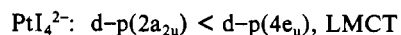
Figure 3. MCD (upper) and absorption spectra of  $\text{PtI}_4^{2-}$ : (a) in  $\text{CH}_3\text{OH}$  and at  $-65^\circ\text{C}$ ; (b) in  $5\text{ M H}_2\text{SO}_4(\text{aq})$  and at  $-50^\circ\text{C}$ . Dotted lines indicate Gaussian bands.

The standard MO diagram<sup>24</sup> displayed in Figure 6 will be used to assign the bands. The two possible alternatives under consideration are



LMCT ligand  $p \rightarrow$  metal  $d$

Calculations<sup>5</sup> and simple crystal field arguments show that the energy of the metal  $p(4e_u)$  orbitals is higher than that of the metal  $p(2a_{2u})$ ; i.e., transitions assigned  $d \rightarrow p(2a_{2u})$  will have lower energies than those assigned  $d \rightarrow p(4e_u)$ . Concerning the relative differences of transition energies of  $d \rightarrow p$  vs. LMCT, the following will be assumed:



In both cases we must in principle consider two alternatives, viz. pure  $d-p$  and LMCT transitions and a mixture of both. However, the measurements on  $\text{PdI}_4^{2-}$  are restricted to  $1/\lambda < 3.8 \mu\text{m}^{-1}$ , so it is only necessary to consider LMCT (vide infra). Concerning

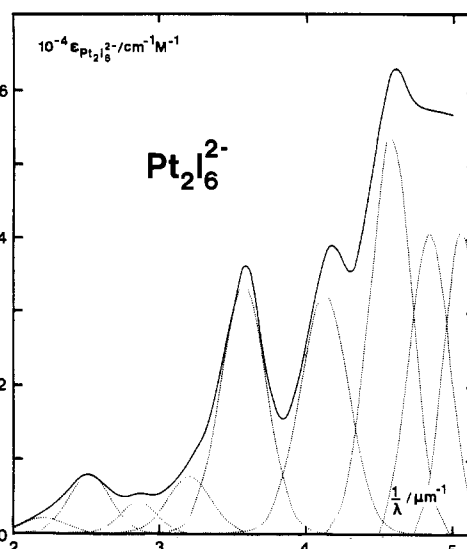


Figure 4. Absorption spectrum of  $\text{Pt}_2\text{I}_6^{2-}$  in  $\text{CH}_3\text{OH}$  and  $-65^\circ\text{C}$ . Dotted lines indicate Gaussian bands.

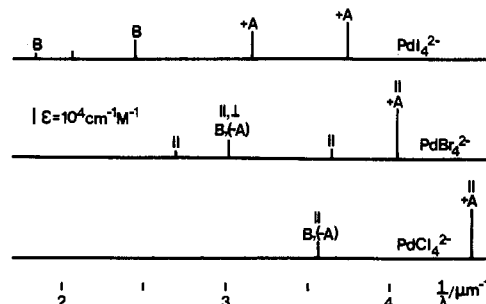


Figure 5. Band positions, MCD terms with signs indicated, and single-crystal polarization data ( $\perp$  denoting transitions perpendicular to and  $\parallel$  denoting transitions parallel to the  $\text{PdX}_4^{2-}$  plane). Data are from ref 3, 4, 6, 11, and 23 and this work.

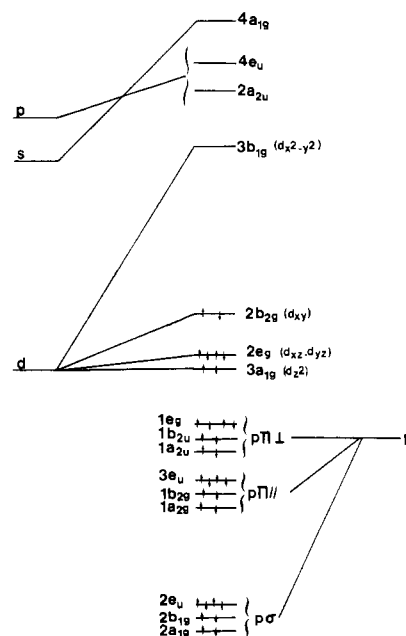


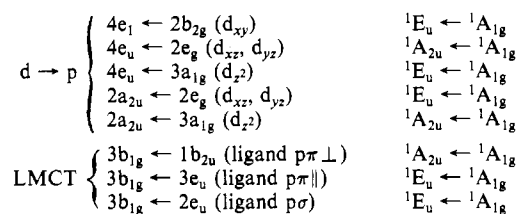
Figure 6. Schematic one-electron MO diagram (from ref 24).

$\text{PtI}_4^{2-}$ , it is possible to have either "pure"  $d \rightarrow p(2a_{2u})$  (low energy) and  $d-p(4e_u)$  or a mixture of these and LMCT. To these possibilities it is also necessary to include singlet-triplet transitions. According to the earlier discussion, it is expected that at least for Pt  $d-p$  and ligand- ( $\text{I}^-$ ) to-metal CT the spin selection rule cannot be assumed to hold. The intensities of these transitions relative

to the singlets can be roughly estimated: the ratio (intensity of singlet-triplet)/(intensity of singlet-singlet) ought to be of the same order of magnitude for metal d-p transitions as for metal d-d transitions. From ref 1 and 6 it can be concluded that the strongest singlet-triplet d-d transition in  $\text{PtCl}_4^{2-}$  has a molar absorptivity approximately one-fourth of that for the corresponding singlet. The corresponding figure for  $\text{PdCl}_4^{2-}$  is approximately one-tenth; cf. ref 6 and 11. Concerning the LMCT transitions, the observed trend between  $\text{PdCl}_4^{2-}$  and  $\text{PdBr}_4^{2-}$  shows<sup>6,11</sup> that transitions to triplet states (in  $\text{PdI}_4^{2-}$ ) ought to give rise to bands with intensities only slightly less than those of the parent singlet states.

Besides the weakening of the spin selection rule, spin-orbit interaction also causes a splitting of triplet states, especially when the "orbital" states are degenerate ( $E_u$ ,  $E_g$ ). Triplet states will be written according to the notation of Isci and Mason;<sup>7</sup> e.g., the two states arising from  $^3E_u$  will be written  $E_u(^3E_u)$ , and  $A_{2u}(^3E_u)$ .

Allowed transitions arising from the assignments discussed above are thus



To these must be added the singlet-triplet transitions. Every transition  ${}^1E_u \leftarrow {}^1A_{1g}$  will have a counterpart at lower energy and with lower intensity:  $E_u(^3E_u) \leftarrow {}^1A_{1g}$ ,  $A_{2u}(^3E_u) \leftarrow {}^1A_{1g}$ , as will  ${}^1A_{2u} \leftarrow {}^1A_{1g}$ ,  $E_u(^3A_{2u}) \leftarrow {}^1A_{1g}$ . This has the following implication: for the bands with "low" intensity in the near-UV/vis region it is necessary to include the singlet-triplet assignment as a realistic alternative. Moreover, for a band in the UV region with "high" intensity there will probably exist satellite band(s) in the former region with "low" intensities. It should be remarked that for LMCT transitions this feature is solely due to the halide ligand but for d-p transitions only the metal atom needs to be considered. This means that if a "mixed" assignment is correct, the pattern found at low energies in  $\text{PdI}_4^{2-}$  (LMCT) must also occur in  $\text{PtI}_4^{2-}$  but at high energies. (The converse (for d-p) is, however, not necessarily true: if the low-energy bands in  $\text{PtI}_4^{2-}$  are of metal d-p singlet-triplet origin, the corresponding bands in  $\text{PdI}_4^{2-}$  will occur at higher energy but with considerably reduced intensities and splitting.)

To summarize, the singlet-singlet metal d-p transitions will correspond to groupings of three and two closely spaced bands, the spacing within each band system being comparable to that of the d-d bands. Both systems ought to be accompanied by bands that can be assigned to singlet-triplet d-p transitions.

Concerning LMCT transitions, the expected trend in the spectra of  $\text{MX}_4^{2-}$  ( $M = \text{Pt}, \text{Pd}$ ;  $X = \text{Cl}, \text{Br}, \text{I}$ ) is that the three singlet-singlet transitions ought to be accompanied by singlet-triplet transitions. The corresponding bands should increase in intensity in the same order as the spin-orbit effect in the halide ions, i.e.,  $\text{Cl}^- < \text{Br}^- < \text{I}^-$ .

Before the assignments of  $\text{PdI}_4^{2-}$  and  $\text{PtI}_4^{2-}$  are discussed separately, a number of similarities and differences between the spectra of the two metal halide complexes will be considered.

**Spectral Changes in the Series  $\text{PtX}_4^{2-}$  and  $\text{PdX}_4^{2-}$  ( $X = \text{Cl}, \text{Br}, \text{I}$ ).** When chloride is substituted by bromide<sup>26</sup> and then by iodide, the symmetry-allowed bands show a marked red shift. The two bands in  $\text{PtCl}_4^{2-}$  at<sup>6</sup> 4.64 and 4.34  $\mu\text{m}^{-1}$  are displaced to<sup>26,27</sup> 3.73 and 3.37  $\mu\text{m}^{-1}$  in  $\text{PtBr}_4^{2-}$  and to 3.02 and 2.58  $\mu\text{m}^{-1}$  in  $\text{PtI}_4^{2-}$  (Figure 1c, all values refer to water as medium). That this group of bands can be identically assigned follows from the similarity

of the molar absorptivities ( $\leq 10^4 \text{ cm}^{-1} \text{ M}^{-1}$ ), the spacing between the bands ( $\approx 0.4 \mu\text{m}^{-1}$ ), and the presence of a broad minimum between these and the following bands, which is clearly discernible in  $\text{PtBr}_4^{2-}$  (cf. ref 7, Figure 2) and  $\text{PtI}_4^{2-}$  (Figure 3a).

Concerning  $\text{PdX}_4^{2-}$ , the two symmetry-allowed bands in  $\text{PdCl}_4^{2-}$  (4.50 and 3.58  $\mu\text{m}^{-1}$ ) are displaced to 4.06 and 3.04  $\mu\text{m}^{-1}$  in  $\text{PdBr}_4^{2-}$  and to 3.74 and 2.45  $\mu\text{m}^{-1}$  in  $\text{PdI}_4^{2-}$ . (That these bands can be identically assigned—as singlet-singlet LMCT—will be shown below.)

Besides the red shift, there is an additional effect of ligand substitution on the spectra of  $\text{PdX}_4^{2-}$ : new bands emerge at the low-energy sides of the symmetry-allowed bands<sup>11</sup> (cf. Figure 5). Thus, the two bands of  $\text{PdCl}_4^{2-}$  (4.50 and 3.58  $\mu\text{m}^{-1}$ ) correspond to two intense bands (4.06 and 3.04  $\mu\text{m}^{-1}$ ) each accompanied by a weak shoulder (3.73 and 2.74  $\mu\text{m}^{-1}$ ) of  $\text{PdBr}_4^{2-}$  and to four intense bands of  $\text{PdI}_4^{2-}$  (3.74, 3.17, 2.45 and 2.07 (1.84)  $\mu\text{m}^{-1}$ ).

A corresponding effect on the spectra of  $\text{PtX}_4^{2-}$  does not exist: the two adjacent bands around 4.5  $\mu\text{m}^{-1}$  in the  $\text{PtCl}_4^{2-}$  spectrum are displaced toward the visible region when chloride is substituted by bromide, but, as remarked by Elding et al. (ref 26, p 14), no new shoulders at the low-energy side are seen in the spectrum of  $\text{PtBr}_4^{2-}$ . This statement holds also for  $\text{PtI}_4^{2-}$ .

Concerning the accompanying changes of the MCD spectra, those of  $\text{PdX}_4^{2-}$  show a consistent trend for  $X = \text{Cl}, \text{Br}, \text{I}$ ; cf. Figure 5. The situation is less clear for  $\text{PtX}_4^{2-}$ , because the interpretations of the MCD spectrum of the two bands of  $\text{PtCl}_4^{2-}$  (ref 3, 7, and 23) partly disagree. According to ref 3 and 7, the one at 4.34  $\mu\text{m}^{-1}$  is connected with a negative  $A$  term, whereas ref 23 suggests a negative  $B$  term. The MCD of the other band (at 4.64  $\mu\text{m}^{-1}$ ) is either associated with a positive  $A$  term<sup>7,23</sup> or stated<sup>3</sup> to be different from that of the bands of  $\text{PdCl}_4^{2-}$ . That both bands should exhibit  $A$  terms seems unlikely. According to the polarized crystal spectrum,<sup>4</sup> one band is out-of-plane polarized. This corresponds to a transition where the upper state is of an  $A_{2u}$  symmetry species. Such a transition cannot give a MCD  $A$  term. The association of a negative  $A$  term with one band is consistent with the MCD of  $\text{PtBr}_4^{2-}$  in  $\text{CH}_3\text{CN}$  (band V of ref 7) and  $\text{PtI}_4^{2-}$  (band II, this work; cf. Table III). There is only one absorption band of  $\text{PdX}_4^{2-}$  that can be associated with a negative  $A$  term; cf. Figure 5 ( $\text{PdCl}_4^{2-}$ , 3.58  $\mu\text{m}^{-1}$ ;  $\text{PdBr}_4^{2-}$ , 3.04  $\mu\text{m}^{-1}$ ). It differs, however, from the relevant band of  $\text{PtX}_4^{2-}$  insofar as it is also connected with a strong, positive  $B$  term. That term will partly ( $\text{PdCl}_4^{2-}$ ,  $\text{PdBr}_4^{2-}$ ) or completely ( $\text{PdI}_4^{2-}$ , band III; cf. Table II and Figure 5) cover the negative  $A$  term (vide infra). It is not possible to draw any safe conclusions from this difference. It only indicates that band II of  $\text{PtI}_4^{2-}$  and band III of  $\text{PdI}_4^{2-}$  do not necessarily need to be identically assigned.

The difference in the spectral features of  $\text{PdX}_4^{2-}$  and  $\text{PtX}_4^{2-}$  shows that the bands with lowest transition energies might have different origins in  $\text{PdX}_4^{2-}$  as compared to  $\text{PtX}_4^{2-}$ . In the former the spectral trend in the series  $X = \text{Cl}, \text{Br}, \text{I}$  is the expected one for LMCT transitions with singlet-triplet included. A different origin for the bands of  $\text{PtX}_4^{2-}$  means that these most probably should be assigned d-p transitions, even though a LMCT assignment for some band cannot be excluded.

Concerning the red shift, it is generally assumed that internal metal transitions are only slightly affected by the ligands. However, a red shift is expected, because the filled d orbitals are subject to the nephelauxetic effect:<sup>28</sup> due to the presence of ligands the metal d orbitals are expanded as compared to their size in the free (nonligated), gaseous metal ion. In ligand field theory the expansion is connected with a decrease in interelectronic repulsion between the metal d electrons in the order of ligands  $\text{Cl}^- < \text{Br}^- < \text{I}^-$ . In this context the essential point is that the increased d-orbital radius corresponds to an increased, i.e. less negative, orbital energy. Thus, the energy gap between the empty metal p and the filled metal d orbitals decreases in the same order of halide ligands.

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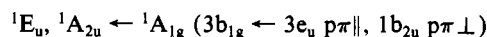
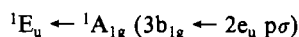
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**Spectral Differences between  $M\text{I}_4^{2-}$  and  $M_2\text{I}_6^{2-}$  ( $M = \text{Pd}, \text{Pt}$ ).** The spectrum of  $\text{Pd}_2\text{I}_6^{2-}$  has been reported previously (ref 9, Figure 1c): the band at  $3.17 \mu\text{m}^{-1}$  ( $\text{PdI}_4^{2-}$ ) corresponds to that at  $3.01 \mu\text{m}^{-1}$  ( $\text{Pd}_2\text{I}_6^{2-}$ ). The intensity is increased by a factor 2.8. For the band at  $2.45 \mu\text{m}^{-1}$  ( $\text{PdI}_4^{2-}$ ) there is no shift either in energy or in intensity; cf. Figure 1b,c of ref 9. The intensity features are probably connected with the different electron distribution in  $M_2\text{I}_6^{2-}$  as compared to that in  $M\text{I}_4^{2-}$ . In the dimer the two bridging ligands must use both of the two sets of in-plane p orbitals for  $\sigma$ -bonding, one set to each of the two palladium atoms. However, the terminal ligands behave as the ligands in the monomer: one set is used for  $\sigma$ -bonding and another for in-plane  $\pi$ -bonding ( $p\pi\parallel$ ); cf. Figure 6; a detailed discussion is given in ref 14.

Concerning  $\text{PtI}_4^{2-}/\text{Pt}_2\text{I}_6^{2-}$  (Figures 3 and 4), the only dramatic change of intensity seems to be connected with the broad absorption around  $3.8 \mu\text{m}^{-1}$  of  $\text{PtI}_4^{2-}$  and  $3.59 \mu\text{m}^{-1}$  of  $\text{Pt}_2\text{I}_6^{2-}$  (band V; cf. Table IV). Both the red shift ( $0.2 \mu\text{m}^{-1}$ ) and the intensity ratio (about 2.5) compare favorably with the pair  $3.17/3.01 \mu\text{m}^{-1}$  of  $\text{PdI}_4^{2-}/\text{Pd}_2\text{I}_6^{2-}$ .

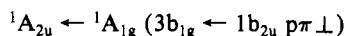
**Assignments.  $\text{PdI}_4^{2-}$ .** The preceding discussion shows that the assignments for the bands of  $\text{PdI}_4^{2-}$  fit well into the established LMCT assignments in  $\text{PdCl}_4^{2-}$  and  $\text{PdBr}_4^{2-}$ . The relevant data for the three complexes are displayed in Figure 5. The two high-intensity bands of  $\text{PdCl}_4^{2-}(\text{aq})$  ( $4.50$  and  $3.58 \mu\text{m}^{-1}$ ) and  $\text{PdBr}_4^{2-}(\text{aq})$  ( $4.06$  and  $3.04 \mu\text{m}^{-1}$ ) are assigned



The accompanying shoulders of  $\text{PdBr}_4^{2-}$  ( $3.73$  and  $2.74 \mu\text{m}^{-1}$ ) are the corresponding singlet-triplet transitions; cf. ref 11, p 2549. Accordingly, in  $\text{PdI}_4^{2-}$  the bands at  $3.74$  and  $2.45 \mu\text{m}^{-1}$  are the singlet-singlet transitions and the accompanying bands with lower energies ( $3.17$  and  $2.07 \mu\text{m}^{-1}$ ) the singlet-triplet transitions. This interpretation for the pair of bands  $2.45, 2.07 \mu\text{m}^{-1}$  seems first to have been suggested by Jørgensen.<sup>25</sup>

The MCD pattern for the suggested singlet-singlet transitions conforms obviously with this assignment. Concerning the suggested singlet-triplet transitions, the band at  $3.17 \mu\text{m}^{-1}$  corresponds to an upper state of  $E_u$  symmetry species (as shown by its MCD  $A$  term, which has the same sign as the band at  $3.74 \mu\text{m}^{-1}$ ). This is expected because of the proximity to the  ${}^1E_u \leftarrow {}^1A_{1g}$  transition.

Concerning the band at  $2.45 \mu\text{m}^{-1}$ , the assignment suggests that this must give rise to an MCD  $A$  term, whereas experiments show only a positive  $B$  term. In the corresponding chloride ( $3.58 \mu\text{m}^{-1}$ ) and bromide ( $3.02 \mu\text{m}^{-1}$ ) complexes there are also positive  $B$  terms accompanied by (a part of) a small negative  $A$  term (the other part is hidden under the much stronger  $B$  term); cf. ref 23, Figure 3 ( $\text{PdCl}_4^{2-}$ ), and ref 3, Figure 5 ( $\text{PdBr}_4^{2-}$ ). The reason for the weak or, in some cases, absent  $A$  term under the bands assigned  $3b_{1g} \leftarrow 3e_u p\pi\parallel$  has been discussed by McCaffery et al.<sup>3</sup> Despite the lack of an  $A$  term, the correctness of the assignment is proved by the single-crystal polarized spectra of  $\text{K}_2\text{PdCl}_4$  and  $\text{K}_2\text{PdBr}_4$ .<sup>11</sup> For the latter complex, Martin et al.<sup>11</sup> have shown that the band at  $3.02 \mu\text{m}^{-1}$  consists of two components. Besides the one discussed above (i.e.  ${}^1E_u \leftarrow {}^1A_{1g} (3b_{1g} \leftarrow 3e_u p\pi\parallel)$ ), there is also an out-of-plane-polarized band that could be unambiguously assigned



The band at  $2.07 \mu\text{m}^{-1}$  has been assigned  ${}^3E_u \leftarrow {}^1A_{1g} (3b_{1g} \leftarrow 3e_u p\pi\parallel)$ . If the upper state is of the  $E_u$  symmetry species, the possible  $A$  term is expected to be very weak, as it is for the singlet-singlet transitions in  $\text{PdCl}_4^{2-}$  ( $3.58 \mu\text{m}^{-1}$ ) and  $\text{PdBr}_4^{2-}$  ( $3.04 \mu\text{m}^{-1}$ ). The band at  $1.84 \mu\text{m}^{-1}$  might be assigned  $E_u ({}^3A_{2u}) \leftarrow {}^1A_{1g} (3b_{1g} \leftarrow 1b_{2u} p\pi\perp)$ , even though its intensity seems to be too high for this (the corresponding singlet-singlet transition in  $\text{PdBr}_4^{2-}$  has a low intensity; cf. ref 11). Possibly it could gain intensity from the  ${}^1E_u \leftarrow {}^1A_{1g}$  transition close to  ${}^1A_{2u} \leftarrow {}^1A_{1g}$ .

**$\text{PtI}_4^{2-}$  and  $\text{Pt}_2\text{I}_6^{2-}$  (Tables III and IV, Figures 3 and 4).** The number of bands in the spectra of these compounds show that the metal d-p assignment (with or without the LMCT one) is necessary for the interpretation.

The preceding discussion shows that there are at least two possible alternative d-p assignment schemes: (i) singlet-singlet d-p( $4e_u$ ) together with d-p( $2a_{2u}$ ); (ii) singlet-singlet and singlet-triplet d-p( $2a_{2u}$ ).

It will be shown below that (i) is less likely than (ii).

(i) To start with, it will be assumed that all d-p singlet-singlet transitions have intensities of "comparable" magnitude. It thus seems hardly reasonable to connect the high-intensity bands in the far-UV region ( $1/\lambda > 4 \mu\text{m}^{-1}$ ) with d-p( $4e_u$ ) and one of the two other band systems ( $4 > 1/\lambda > 3.3$  and  $1/\lambda < 3.2 \mu\text{m}^{-1}$ ) with d-p( $2a_{2u}$ ). Rather, the intensities of these last two band systems indicate that the one at lower energy ( $1/\lambda < 3.2 \mu\text{m}^{-1}$ ) hypothetically can be assigned d-p( $2a_{2u}$ ) and the other system d-p( $4e_u$ ). However, such an assignment can be rejected for several reasons.

1. Sign of a MCD  $A$  term: With d-p( $2a_{2u}$ ) such a term can only be connected with  ${}^1E_u \leftarrow {}^1A_{1g} (2a_{2u} \leftarrow 2e_g)$ . It has been demonstrated by Stephens et al.<sup>29</sup> that this transition must give rise to a positive MCD  $A$  term. In the low-energy spectrum there is only a band with a negative  $A$  term, viz.  $2.54 \mu\text{m}^{-1}$  ( $\text{PtI}_4^{2-}$ ).

2. Accompanying singlet-triplet transitions: Such are expected, having intensities about 5 times smaller than the parent singlet-singlet transitions ( $\epsilon_{\text{max}} \approx 10^3 \text{ cm}^{-1} \text{ M}^{-1}$ ) and transition energies below, e.g.,  $2 \mu\text{m}^{-1}$  (for d-p( $2a_{2u}$ )). Obviously, there are no corresponding bands in the spectrum of  $\text{PtI}_4^{2-}$ .

3. Spectral differences between  $\text{PtI}_4^{2-}$  and  $\text{Pt}_2\text{I}_6^{2-}$ : The intensities of the low-energy bands of  $\text{PtI}_4^{2-}$  are only slightly different from those of  $\text{Pt}_2\text{I}_6^{2-}$ . On the contrary, the intensity of one of the bands between  $3.3$  and  $4 \mu\text{m}^{-1}$  differs considerably. Thus, the two-band systems can hardly both be of d-p origin.

4. The far-UV bands ( $1/\lambda > 4 \mu\text{m}^{-1}$ ): If these bands not are assigned d-p transitions, they must of course be assumed to be of the LMCT type and thus similar to the bands of  $\text{PdI}_4^{2-}$ . However, the bands of this latter complex have much lower intensities. In addition, the spectral features of the far-UV bands of  $\text{PtI}_4^{2-}/\text{Pt}_2\text{I}_6^{2-}$  are different from those of the strongest bands of  $\text{PdI}_4^{2-}/\text{Pd}_2\text{I}_6^{2-}$ .

From the arguments presented under points 3 and 4, it follows that the far-UV bands might better be described as d-p transitions but that at least one of the bands in the broad absorption between  $3.3$  and  $4 \mu\text{m}^{-1}$  may correspond to a LMCT transition (vide infra). Also, the earlier discussion about the spectral changes of  $\text{PtX}_4^{2-}$  and  $\text{PdX}_4^{2-}$  shows that the bands of  $\text{PtI}_4^{2-}$  with lowest transition energies reasonably are of the d-p type.

(ii) The discussion above shows that the high-intensity band system in the right part of Figure 3 ( $1/\lambda > 4 \mu\text{m}^{-1}$ ) together with the low-intensity band system to the left ( $1/\lambda < 3.2 \mu\text{m}^{-1}$ ) hypothetically can be assigned as a d-p singlet-singlet system and its accompanying singlet-triplet. The intensity ratio (vide earlier discussion) is  $\leq 1/4$ . This compares well with that for the internal metal d-d bands but *not* with that for the LMCT bands of  $\text{PdI}_4^{2-}$ .

A possible assignment would thus be that two of the bands with  $1/\lambda > 4 \mu\text{m}^{-1}$  can be assigned d-p( $2a_{2u}$ ) singlet-singlet. The presence of a positive MCD  $A$  term (connected with band VII; cf. Table III) conforms with this assignment ( $2a_{2u} \leftarrow 2e_g$ ). The d-p( $2a_{2u}$ ) assignment can only explain the presence of two bands. The third band (possibly the one with highest energy) can hypothetically be assigned as one of the three singlet-singlet d-p( $4e_u$ ) bands or, alternatively, all three bands may be connected with this latter assignment. That would mean, however, that the  $2a_{2u}$  level has a higher energy than  $4e_u$ , which seems rather unlikely.<sup>5</sup> (Such a possibility has been discussed by Kozelka.<sup>30</sup>) Even a CTTS (charge-transfer-to-solvent) transition can explain the presence of a third band.

Finally, the bands around  $3.85 \mu\text{m}^{-1}$  (Figure 3a) will be considered. From the corresponding spectrum in  $5 \text{ M H}_2\text{SO}_4(\text{aq})$ , Figure 3b, the band at  $4.01 \mu\text{m}^{-1}$  (probably connected with a positive MCD  $A$  term) can possibly be assigned as the LMCT

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$E_u(^3E_u) \leftarrow ^1A_{1g}(3b_{1g} \leftarrow 2e_u p\sigma)$ . This band should occur around  $3.85 \mu\text{m}^{-1}$  in  $\text{CH}_3\text{OH}$  (Figure 3a) and be connected with the strong band at lower energy in  $\text{Pt}_2\text{I}_6^{2-}(\text{CH}_3\text{OH})$ , viz.  $3.59 \mu\text{m}^{-1}$  (Figure 4), because both the change in transition energy and the intensity ratio between these bands are very similar to those of  $\text{PdI}_4^{2-}/\text{Pd}_2\text{I}_6^{2-}$  ( $3.17/3.01 \mu\text{m}^{-1}$ ). Hypothetically, the bands at 3.76 and  $3.63 \mu\text{m}^{-1}$  ( $\text{PtI}_4^{2-}$ , 5 M  $\text{H}_2\text{SO}_4(\text{aq})$ ) can then be assigned  $^1E_u$ ,  $^1A_{2u} \leftarrow ^1A_{1g}(3b_{1g} \leftarrow 3e, b_{2u})$  and its corresponding singlet-triplet (compare  $2.45$  and  $2.07/1.84 \mu\text{m}^{-1}$  for  $\text{PdI}_4^{2-}$  in Table II and Figure 2). It is obvious that arguments against these assignments can be inferred both from the smaller band spacing (about  $0.3 \mu\text{m}^{-1}$ ) in  $\text{PtI}_4^{2-}$  but more than twice that in  $\text{PdI}_4^{2-}$  ( $3.17 \mu\text{m}^{-1} - 2.45 \mu\text{m}^{-1} = 0.72 \mu\text{m}^{-1}$ ) and also from the different MCD ( $B$ -term) features; cf. Figure 2 ( $1/\lambda < 2.7 \mu\text{m}^{-1}$ ) and Figure 3. (That there should be some difference in the  $B$  terms connected with LMCT transitions in  $\text{PtI}_4^{2-}$  as compared to those for  $\text{PdI}_4^{2-}$  is expected. One of the important factors is the proximity of states of correct symmetry,<sup>22</sup> and the energy differences between states derived from metal  $d$ - $p$  configurations and those derived from ligand  $p$ -metal  $d(3b_{1g})$  configurations are considerably smaller in  $\text{PtI}_4^{2-}$  than in  $\text{PdI}_4^{2-}$ .)

The assignment alternative (ii) has been included in Table III. Because it is uncertain and other probable alternatives exist, the

individual bands have not been assigned.

## Conclusions

The spectra and spectral assignments presented in this and other studies show that the internal metal  $d$ - $p$  assignment is well established for the  $\text{PtX}_4^{2-}$  spectra ( $X = \text{Cl}, \text{Br}, \text{I}$ ). The presence of LMCT transitions suggested<sup>7</sup> to occur besides the  $d$ - $p$  transitions seems also justified. Obviously, a number of details are still obscure. It would be highly desirable to get spectral information from single-crystal polarization measurements and to penetrate the UV spectral region for  $\text{PdI}_4^{2-}$  and  $\text{Pd}_2\text{I}_6^{2-}$  both by absorption and MCD measurements.

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**Registry No.**  $\text{PdI}_4^{2-}$ , 16182-47-1;  $\text{PtI}_4^{2-}$ , 14349-66-7;  $\text{Pt}_2\text{I}_6^{2-}$ , 45632-38-0.

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## Anisotropic Exchange Interactions in the Copper(II) and Vanadium(IV) Dimers $[(L')\text{Cu}(\mu\text{-OH})_2\text{Cu}(L')](\text{ClO}_4)_2$ and $[(L)\text{VO}(\mu\text{-OH})_2\text{VO}(L)]\text{Br}_2$ with 1,4,7-Triazacyclononane (L) and Its $N,N',N''$ -Trimethyl Derivative (L'): A Single-Crystal EPR Study

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The zero-field-splitting tensors for the spin-triplet states of Cu(II) and V(IV) dimers in the compounds  $[(L')\text{Cu}(\mu\text{-OH})_2\text{Cu}(L')](\text{ClO}_4)_2$  (Ia) and  $[(L)\text{VO}(\mu\text{-OH})_2\text{VO}(L)]\text{Br}_2$  (II) have been deduced from the results of EPR single-crystal and powder experiments. Parameters for Ia:  $|D| = 0.9250 \text{ cm}^{-1}$ ,  $|E| = 0.0514 \text{ cm}^{-1}$ ;  $g_z^c \approx 2.25$ ,  $g_y^c \approx g_x^c \approx 2.06$ . Parameters for II:  $|D| = 0.0037 \text{ cm}^{-1}$ ,  $|E| = 0.0472 \text{ cm}^{-1}$ ;  $g_z^c = 1.946$ ,  $g_y^c = 1.975$ ,  $g_x^c = 1.988$ ;  $A_z^c = 76 \times 10^{-4} \text{ cm}^{-1}$ ,  $A_y^c = 32 \times 10^{-4} \text{ cm}^{-1}$ ,  $A_x^c = 23 \times 10^{-4} \text{ cm}^{-1}$ . The derived anisotropic exchange contributions to  $D$  and  $E$  allowed estimation of the exchange integrals  $J_{x^2-y^2,xy}$ , which are of similar magnitude for Ia ( $\approx -510 \text{ cm}^{-1}$ ) and II ( $\approx -410 \text{ cm}^{-1}$ ), as expected. In contrast, published values for the exchange integrals, which were calculated from magnetic susceptibility data, are very different, namely  $J_{x^2-y^2,x^2-y^2} \approx 90 \text{ cm}^{-1}$  for Ia and  $J_{xy,xy} \approx 354 \text{ cm}^{-1}$  for II. The latter implies a direct  $d_{xy^1-d_{xy^1}}$  interaction, while the former describes a  $d_{x^2-y^2^1-d_{x^2-y^2^1}}$  superexchange interaction via the bridging oxygen atoms. Results for the green isomer Ib of the blue dimer Ia, which has a  $S = 1$  ground state as opposed to the case for Ia and II, are also given.

## Introduction

The nature of the exchange interactions in binuclear hydroxo-bridged transition-metal complexes has been the subject of many papers published in the last 30 years. Correlations between the structure of the dimers and the energy and type of the isotropic exchange coupling were experimentally established<sup>1</sup> and explained by suitable theoretical models.<sup>2-5</sup> The anisotropic exchange effects, which contribute to the zero-field splitting of dimeric compounds, have been studied intensively only in the last few years.<sup>5-8</sup> Though mainly copper complexes have been studied, a paper dealing with a hydroxo-bridged chromium dimer recently appeared.<sup>9</sup> We will present below the results of a spectroscopic study of binuclear bis( $\mu$ -hydroxo)-bridged complexes, which were prepared and characterized by Wieghardt and co-workers.<sup>10,11</sup> The copper(II) dimer  $[(L')\text{Cu}(\text{OH})_2\text{Cu}(L')](\text{ClO}_4)_2$  with the tridentate ligand  $N,N',N''$ -trimethyl-1,4,7-triazacyclononane (L') exists in two isomeric forms.<sup>10</sup> While the blue isomer (Ia) is

structurally well-characterized with a symmetrical bis( $\mu$ -hydroxo) bridge (Figure 1, Table I), the green isomer (Ib) seems to exhibit disorder within the unsymmetrical bridge, with possibly an oxo and  $\text{H}_2\text{O}$  ligand. The  $\text{Cu}^{2+}$  ions are five-coordinated, and the geometry corresponds to a strongly elongated square pyramid. This structural feature is in accord with predictions by a vibronic

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