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Electronic Spectra and Photochemistry of Methyl Platinum(IV) Complexes

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Abstract

The absorption and emission spectra as well as the photochemistry of the platinum(IV) methyl complexes $[Pt(CH_3)_3I]_4$ and $[Pt(bipy)(CH_3)_3I]$ are reported and discussed. The compounds show photoemission from ligand field and intraligand excited states, respectively, and undergo reductive eliminations to platinum(II) from ligand to metal charge transfer states which occur at higher energies.

INTRODUCTION

The photochemistry of metal alkyl complexes has been investigated extensively during the last 15 years [1-3]. While much information has been accumulated on the photoproperties of such compounds with metals in low oxidation states much less is known about the light sensitivity of alkyl complexes which contain the metal in higher oxidation states. The importance of this subject has been emphasized in our recent study of the photochemistry of CH_3ReO_3 [4]. As an extension we started to investigate the photoproperties of Pt(IV) methyl complexes. Some reports on the photochemistry of complexes which contain the $Pt(IV)(CH_3)_3$ moiety have been published before. Especially Puddephatt and his group analyzed the photoproducts of compounds such as $[Pt(bipy)(CH_3)_3I]$ [5] and $[Pt(bipy)(CH_3)_4]$ [6] with bipy = 2,2′-bipyridine. In addition, others observed the photosensitivity of $[Pt(CH_3)_3(ClO_4)]_4$ [7] and $[Pt(CH_3)_3C_5H_5]$ [8]. However, it is quite surprising that these studies contain only little information on the electronic absorption and emission spectra which are of general importance for the understanding of the photochemistry. While some Pt(IV) complexes are known to be luminescent [9] an emission of Pt(IV) methyl complexes has not been reported before. It follows from these considerations that the investigation of the photoproperties of platinum(IV) methyl complexes should be of general interest. We explored this possibility and selected the compounds $[Pt(CH_3)_3I]_4$ and $[Pt(bipy)(CH_3)_3I]$ for the present study. A further interesting aspect of the complex $[Pt(CH_3)_3I]_4$ concerns the nature of the metal-metal interaction in the ground and electronically excited state. The emission behavior of related tetrameric d^{10} metal complexes with similar structural features has been investigated quite recently [10]. Finally, as a point of historical interest it should be mentioned that $[Pt(CH_3)_3I]_4$ was the first transition metal σ-organyl complex ever reported [11].

EXPERIMENTAL

The compounds $[Pt(CH_3)_3I]_4$ [12,13] and $[Pt(bipy)(CH_3)_3I]$ [14] were preprared according to published procedures. Absorption spectra were measured in solution at room temperature on a Shimadzu UV-2100 absorption spectrometer. Emission and excitation spectra of the compounds in the solid state, in solution or in toluene glasses (77 K) were obtained on a Hitachi 850 spectrofluorimeter equipped with a Hamamatsu R 928 photomultiplier. The photolysis procedures have been described elsewhere [15]. Gaseous products (CH_4 and C_2H_6) were identified by gas chromatography (Perkin Elmer 8500).

RESULTS

Electronic Spectra

The cluster $[Pt(CH_3)_3I]_4$ is slightly soluble in organic solvents. In hexane the absorption spectrum (Fig. 1) displays bands at λ_{max} = 209 nm (ε = 90 200) and 436 nm (20). At 77 K a red emission of moderate intensity at λ_{max} = 735 nm was observed for $[Pt(CH_3)_3I]_4$ in the solid state or in glasses of toluene (Fig. 1). At room temperature this emission was quite weak. The excitation spectrum matched the absorption spectrum rather well.

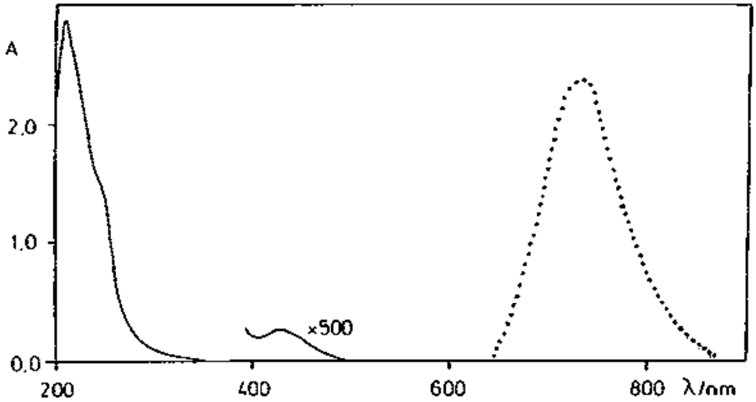


Figure 1. Electronic absorption (——) and emission (···) spectra of $[Pt(CH_3)_3I]_4$. Absorption: 3.18×10^{-5} M in n-hexane at room temperature, 1 cm cell. Emission: in toluene at 77 K; λ_{exc} = 350 nm, intensity in arbitrary units.

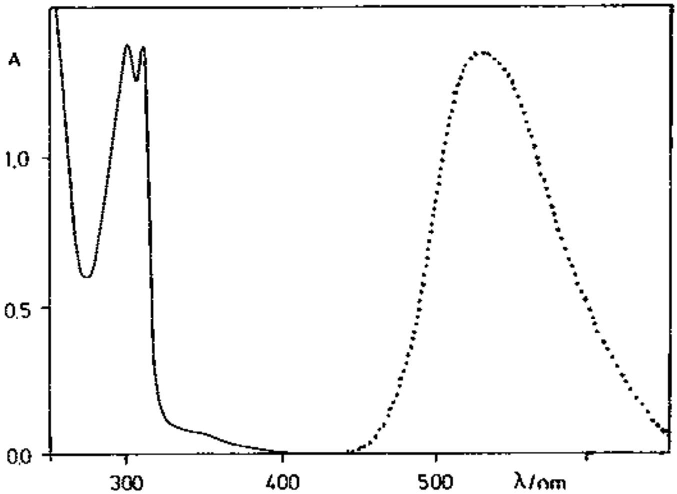


Figure 2. Electronic absorption (——) and emission (···) spectra of $[Pt(bipy)(CH_3)_3I]$ in ethanol at room temperature; 1 cm cell. Absorption: 1.16×10^{-4} M. Emission: $\lambda_{exc.}$ = 350 nm, intensity in arbitrary units.

The mononuclear complex [Pt(bipy)$(CH_3)_3$I] is also soluble in organic solvents. In ethanol the absorption spectrum (Fig. 2) exhibits bands at λ_{max} = 298 nm (ε = 11 900), 310 nm (11800), and 343 nm (700, sh). At room temperature solutions of the complex showed a rather strong yellow-green emission at λ_{max} = 528 nm (Fig. 2) even in aerated solutions. Due to the photolysis of this compound the emission intensity decreased upon exposure of the solution to the exciting light of the emission spectrometer. Again, the excitation spectrum of [Pt(bipy)$(CH_3)_3$I] agreed quite well with the absorption spectrum.

Photochemistry

Solutions of $[Pt(CH_3)_3I]_4$ were light sensitive. The photolysis of the complex in hexane was accompanied by spectral changes (Fig. 3) which

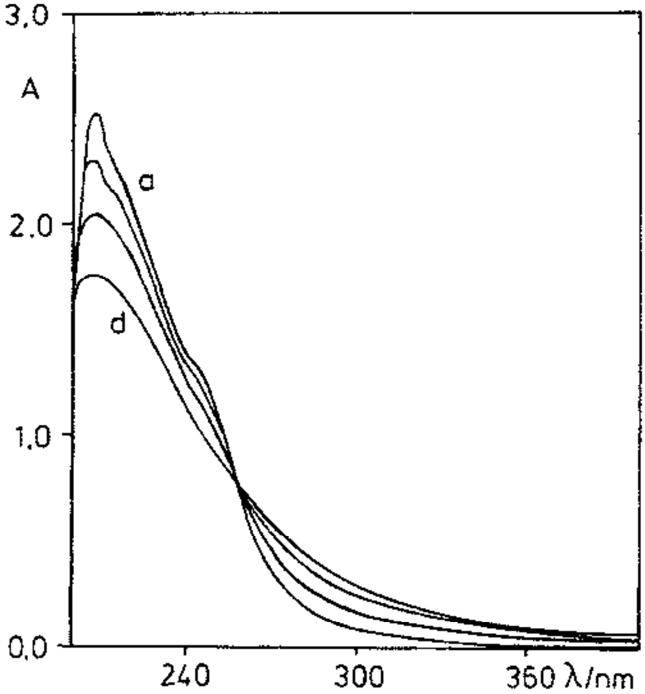


Figure 3. Spectral changes during the photolysis of 2.82×10^{-5} M $[Pt(CH_3)_3I]_4$ in n-hexane at (a) 0, 3, 8, and (d) 20 min irradiation time, with λ_{irr} = 254 nm and a 1 cm cell.

include a clear isosbestic point at 257 nm. This spectral pattern was preserved only in the beginning. Later, a secondary photolysis and possibly thermal reactions led to the disappearance of this isosbestic point and to a precipitation of a brownish material which became darker upon prolonged irradiation. The primary photolysis of $[Pt(CH_3)_3I]_4$ in hexane/ethanol (1:1) yielded methane, very little ethane, and a labile complex which was assumed to be $[Pt(CH_3)I]$. This assumption is based on the observation that upon addition of bipy to photolyzed solutions the complex $[Pt(bipy)(CH_3I]$ was immediately formed and identified by its absorption spectrum (λ_{max} = 417 nm) [16]. Due to analytical problems a reliable absolute quantum yield for the photolysis of $[Pt(CH_3)_3I]_4$ could not be determined. However, relative wavelength-dependent quantum yields were obtained. At λ_{irr} = 254 nm the photolysis of $[Pt(CH_3)_3I]_4$ in hexane was about 90 times more efficient than that at λ_{irr} = 436 nm.

The photolysis of $[Pt(bipy)(CH_3)_3I]$ in organic solvents by UV light has been studied before. Puddephatt et al. observed a reductive elimination. We could confirm this observation. The spectral variations which accompanied the irradiation (Fig. 4) indicated the formation of

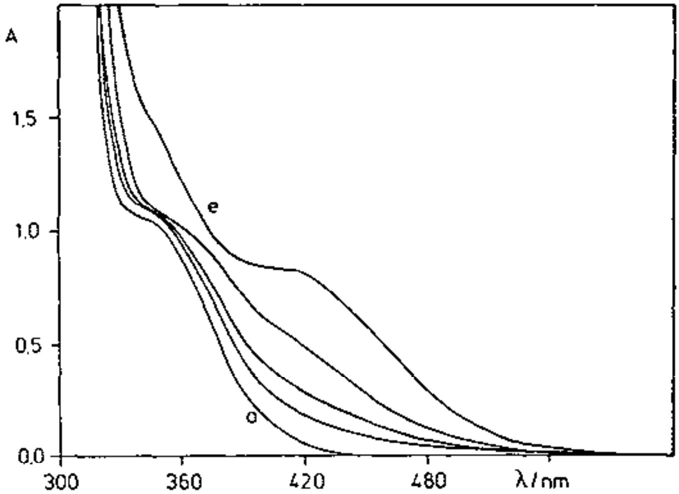


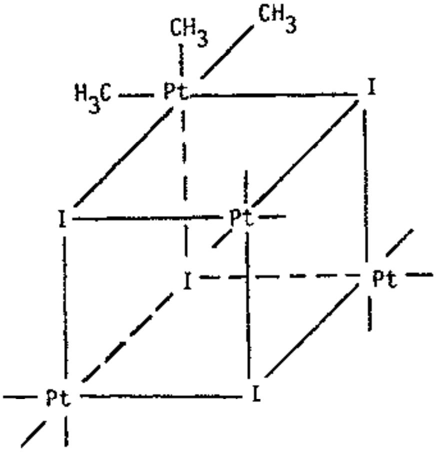
Figure 4. Spectral changes during the photolysis of 1.53×10^{-3} M $[Pt(bipy)(CH_3)_3I]$ in n-hexane/ethanol (1:1) at (a) 0, 4, 10, 20, and (e) 80 min irradiation time, with λ_{irr} = 366 nm and a 1 cm cell.

[Pt(bipy)(CH_3)I] [16]. Based on the spectral changes quantum yields were determined (ϕ = 0.05 at λ_{irr} = 254 nm and ϕ = 0.01 at λ_{irr}= 366 nm).

DISCUSSION

Electronic Spectra

Generally platinum(IV) with a d^6 electron configuration forms octahedral complexes. The tetrameric cluster $[Pt(CH_3)_3I]_4$ contains four pseudooctahedral (C_{3v}) fac-$[Pt(CH_3)_3I_3]$ components which are interconnected by a Pt_4I_4 cubane structure [17].



The electronic spectra are discussed on the basis of a pseudooctahedral $[Pt(CH_3)_3I_3]$ complex which is perturbed by the electronic metal-metal interaction in the cluster. Since CH_3^- is a strong field and I^- a weak-field ligand [18] and both ligands are trans standing, ligand field (LF) bands are expected to appear at intermediate energies. The longest-wavelength LF band (Fig. 1) at λ_{max} = 436 nm which is assigned to the spin-forbidden $t_{2g} \rightarrow e_g$ transition (in O_h symmetry, see the simplified MO scheme, Fig. 5) appears in a wavelength region which is also characteristic for ^{3}LF bands of other Pt(IV) complexes [9,18]. This transition may be modified by metal-metal interaction in the cluster which is essentially achieved by the overlap of the t_{2g} orbitals (in O_h or a_1+2e orbitals in C_{3v} symmetry). These d orbitals are thus split into six a_1+e+t_2

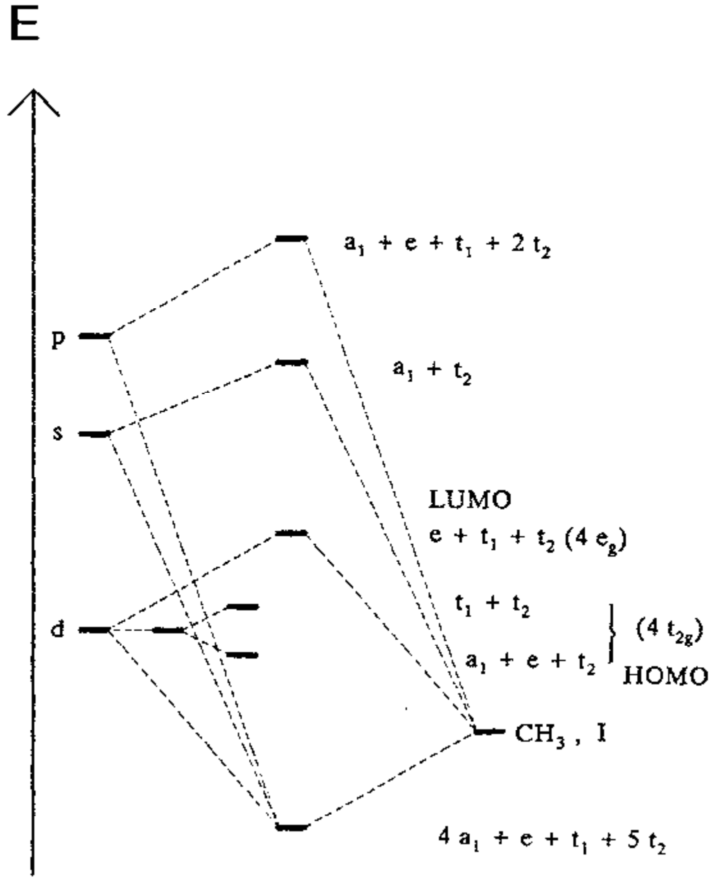


Figure 5. Qualitative MO scheme of $[Pt(CH_3)_3I]_4$ (in T_d symmetry) and its mononuclear component fac-$[Pt(CH_3)_3I_3]$ (in O_h symmetry).

bonding and six t_1+t_2 antibonding MOs (in T_d symmetry of the cluster) [19]. Since the LF band of $[Pt(CH_3)_3I]_4$ at 436 nm appears in the same energy range as that of other Pt(IV) complexes it is assumed that in the ground state the metal-metal interaction and hence the splitting of the t_{2g} orbitals is small.

The emission of $[Pt(CH_3)_3I]_4$ at λ_{max} = 735 nm is suggested to originate from the lowest LF triplet. However, the Stokes shift of this transition ($\Delta\bar{\nu}$ = 9 330 cm^{-1}) is clearly larger than that of other Pt(IV) complexes [9]. We assume that this is due to the metal-metal interaction in the electronically excited cluster. The LF transition is associated with the removal of an electron from the t_1+t_2 orbitals which are antibonding with regard to the Pt_4 tetrahedron. In addition, the LF transition leads to the population of the e_g (or e+t_1+t_2 in T_d symmetry) orbitals which are antibonding with respect to the metal-ligand bonding. It follows that in the LF excited state th Pt_4I_4 cubane structure should distort by a contraction of the Pt_4 and an expansion of the I_4 tetrahedron. Such a distortion can now explain the larger Stokes shift for the LF emission of $[Pt(CH_3)_3I]_4$ compared to that of other Pt(IV) complexes.

The intense absorption bands of $[Pt(CH_3)_3I]_4$ at shorter wavelength are assigned to LMCT transitions in accordance with the reducing character of the ligands and the oxidizing nature of Pt(IV).

The absorption spectrum of $[Pt(bipy)(CH_3)_3I]$ (Fig. 2) is dominated by the fairly intense intraligand (IL) bands at λ_{max} = 298 and 310 nm which are assigned to the spin-allowed $^1\pi\pi^*$ transition of the coordinated bipy. An additional much weaker band at λ_{max} = 343 nm belongs certainly to the spin-forbidden $^3\pi\pi^*$ IL transition which was also detected in the spectrum of $[Ir(bipy)_3]^{3+}$ [20]. Less intense LF bands of $[Pt(bipy)(CH_3)_3I]$ are not observed but are expected to occur at higher energies than the IL bands since with the exception of the iodide all other ligands are of the strong-field type [18]. Absorptions which appear below 275 nm are assigned to LMCT transitions. As an alternative, these bands may belong to ligand to ligand charge transfer (LLCT) transitions from the methyl ligands (Pt-C σ-bond) to the bipy π^* orbitals. Puddephatt et al. suggested such an assignment for the long-wavelength absorptions of $[Pt(bipy)(CH_3)_4]$ [6].

The assumption that the lowest excited state of $[Pt(bipy)(CH_3)_3I]$ is indeed of the IL type is confirmed by the emission (Fig. 2) which clearly originates from the bipy $^3\pi\pi^*$ state. This luminescence appears at the same energy as the IL phosphorescence of other bipy complexes [9,20] including those of Zn^{2+} [21]. In addition, a LF assignment to the emission of $[Pt(bipy)(CH_3)_3I]$ can be ruled out since LF emissions of Pt(IV) complexes do not occur in solution at room temperature [9]. The complex $[Pt(bipy)(CH_3)_3I]$ is thus a unique example of a bipy Pt(IV) complex which shows a luminescence under ambient conditions. Other complexes such as $[Pt(bipy)_2Cl_2]^{2+}$ undergo this IL phosphorescence only at low temperatures [9]. In this case the LF states may be located only slightly above the IL states which are then thermally quenched at room temperature. However, Pt(IV) complexes with ortho-metallated ligands which are related to bipy have been also reported to emit an IL phosphorescence under ambient conditions [22].

Photochemistry

The tetrameric complex $[Pt(CH_3)_3I]_4$ consists of monomeric components which undergo a photochemical reductive elimination:

$$[Pt(IV)(CH_3)_3I] \rightarrow [Pt(II)(CH_3)I] + 2\cdot CH_3$$

The methyl ligands are not cleaved off as ethane in a concerted fashion but are released as methyl radicals which abstract hydrogen from the solvent e.g. ethanol. Accordingly, methane is formed as a photoproduct. Both methyl radicals may be eliminated in two consecutive steps generating $[Pt(III)(CH_3)_2I]$ as an intermediate. The final photoproduct $[Pt(II)(CH_3)I]$ is apparently not stable but can be stabilized as $[Pt(bipy)(CH_3)I]$ upon addition of bipy.

The reactive excited state of $[Pt(CH_3)_3I]_4$ is certainly of the LMCT type. LF excitation at lower energies does not initiate the reductive elimination.

The products of the secondary photolysis of $[Pt(CH_3)_3I]_4$ were not identified, but the dark precipitate seems to be platinum metal which could be formed by a further reductive elimination from $[Pt(CH_3)I]$. A photochemical generation of platinum metal by a four-electron reduction of Pt(IV) has been observed before [23,24].

The complex $[Pt(bipy)(CH_3)_3I]$ undergoes also a photochemical reductive elimination:

$$[Pt(IV)(bipy)(CH_3)_3I] \rightarrow [Pt(II)(bipy)(CH_3)I] + 2\cdot CH_3$$

The photoreaction is initiated most likely by a LMCT (or LLCT) state which can be excited directly by short-wavelength irradiation or populated thermally from bipy IL states at lower energies. However, the quantum yield of reductive elimination is greatly reduced upon irradiation of the IL bands at longer wavelength.

In conclusion, we believe that the present work contributes to a better understanding of the photochemistry of platinum(IV) complexes. While a large number of Pt(IV) compounds [23-25] including organometallics [1-3] such as methyl complexes [5-8] have been found to undergo photochemcial reductive eliminations, a complete insight into the excited state processes has not yet been achieved.

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