fluence of platinum atoms is sensitive to the mode of acetylene bridging.

A few calculations have been accumulated so far on the electronic structures of acetylene-bridged dinuclear complexes.[31-34] Recently, the reactivity of an acetylene-bridged dinuclear nickel complex toward dihydrogen was interpreted in terms of the lobe shape of some molecular orbitals.[35] The present approach of elucidating the characteristics of key orbitals, on the basis of the nuclear spin–spin coupling constants will, therefore, not only assist the interpretation of bonding properties but also provide a practical clue to the design of orbital-controlled reactions.[36]

Registry No. 1, 72207-39-7; **4**, 79084-40-5; **5**, 79084-41-6; **6**, 79084-42-7; **8**, 79084-43-8; $Pt_2(CO)_2(PPh_3)_2(EtOOCC\equiv CCOOEt)$, 79084-44-9; $[PtCH_3(PH_3)_3]^+$, 79084-45-0; $[PtH(PH_3)_3]^+$, 79084-46-1.

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Vibronic Structure of Square-Planar Complexes. Some Evidence of Odd Mode Progressions

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Recent theoretical work contends that progressions in odd modes, rather than in totally symmetric modes, comprise the band structure in electronic transitions of metal complexes. Evidence supporting this hypothesis is provided by the luminescence spectrum of $[Pt(bpy)Cl_2]$ and by reexamination of luminescence data on $PtCl_4^{2-}$.

Introduction

It is fairly generally acknowledged that the structure of spectral bands due to electronic transitions, of transition-metal complexes as well as other molecules, results from vibronic progressions in one or more normal modes which are totally symmetric or at least totally symmetric in the point group of the final state.[1,2] There is indeed an impressive amount of evidence, experimental[3-11] and theoretical,[8,12-14] for this assumption. The experimental evidence includes some very careful spectroscopic work on metal complexes doped in host crystals at low temperatures, in which the vibronic components are quite distinct, and in which the individual progression frequencies may be determined. This work has supported well the statement above.

In a recent paper by Hollebone,[15] however, the group theoretical foundations of this hypothesis have been called into question. Hollebone has contended that it is incorrect, or, at least, insufficient, to analyze the vibronic problem in terms of the static symmetry of the molecule in its equilibrium position. In the equilibrium position, a d–d transition is forbidden. The transition must therefore occur from a nonequilibrium position, in which the molecule has a lower symmetry, and consequently the problem becomes a dynamic one in which displacements (in initial as well as final states) along all the normal coordinates are considered, and the Born–Oppenheimer approximation is explicitly rejected.

The continuous group of three-dimensional harmonic motions may be taken to be SU(3), the group of unitary, unimodular 3 × 3 matrices.[15] Electronic wavefunctions may be formulated in terms of the group SU(2), which corresponds to the labeling of wavefunctions according to the free ion terms from which they are derived. The appropriate group in which to classify vibronic wavefunctions should then be SU(2) × SU(3), or SU(6). This is restricted by Hollebone to SU(3).[15]

Within this framework, the operative principle is an octupole selection rule for the total wavefunction (dipole and quadrupole interactions are forbidden), i.e., the quantum number associated with the representation in SU(3) of the wavefunctions in question must change by 3 (actually 3 mod 4) during a transition from one state to another. This may be expressed as

$$|\Delta L| + |\Delta S| + |\Delta V| = 3 \qquad (1)$$

In this equation, S and L are the normal spin and orbital angular momentum quantum numbers, and V is a quantum number (not to be confused with v, the number of excited vibrational quanta) determined from the SU(3) representation of the vibrational part of the wavefunction. V may be obtained by inspection as the number of nodes associated with a spatial representation of a particular normal mode. For example, the v_4 asymmetric stretch of a planar AB_4 molecule, as with an

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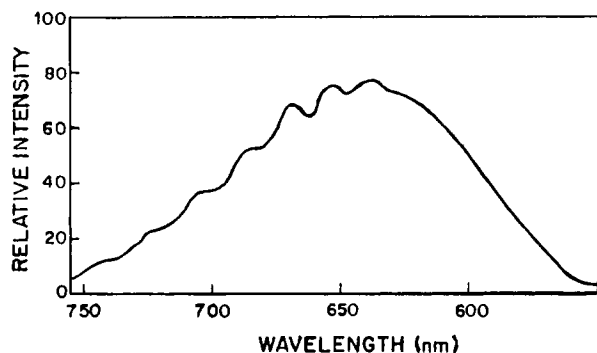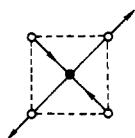
Figure 1. Luminescence spectrum of [Pt(bpy)Cl₂] at 12 K.

analogous d orbital, has two perpendicular planar nodes, so that $V = 2$.

Not surprisingly, V is even for gerade modes and odd for ungerade. In general, only one value of V in the final-state wavefunction will satisfy eq 1, and this selection rule proves to be more stringent than that derived from the static model. In addition, the selection rule specifies not just the symmetry of the vibrational part of the final state wavefunction, but, a fortiori, the direction in normal coordinate space along which the molecule in the final state is extended.[15]

Hollebone's model thus makes specific predictions about the normal mode(s) responsible for the structure of spectral bands in absorption and luminescence. In general, these mode(s) are *not* the totally symmetric ones and are in fact odd in molecules with a center of symmetry, a conclusion reached on occasion by others.[16] It is thus necessary to reexamine old data and interpret new, in light of these two starkly contradictory models. Luminescence spectra are most useful for this purpose because the vibrational structure can be associated with the ground state and compared with infrared and Raman data. In this paper we examine some previously published data on square-planar complexes. We also present new data on the complex [Pt(bpy)Cl₂], where bpy = bipyridine, including low-temperature luminescence and far-infrared spectra. This complex is somewhat unusual in exhibiting vibronic structure at 12 K without doping into a host lattice.

Experimental Section

Yellow [Pt(bpy)Cl₂] was purchased from Strem Chemical and was recrystallized from water. A known red modification was also synthesized but exhibited no vibronic structure.

Luminescence spectra were obtained on an apparatus based on a Spex 1400-II 0.75-m double monochromator and an ITT FW-130 photomultiplier tube (extended S-20). dc amplification was used, and excitation was with a 500-W mercury lamp and an Instruments SA H-10 monochromator. The sample was refrigerated to 12 K in an Air Products Displex CSA-202 cryostat.

Far-infrared spectra were obtained on polyethylene pellets with a Beckman FIR-720 interferometer.

Results

The luminescence spectrum at 12 K of [Pt(bpy)Cl₂] is illustrated in Figure 1, while the peak positions are listed in Table I. The average separation of the six central peaks (the most distinct) is 320 cm⁻¹. This figure corresponds closely to reported Pt–Cl stretching frequencies.[17-21]

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Table I. Vibronic Peak Positions in the 12 K Luminescence Spectrum of [Pt(bpy)Cl₂]

max, cm⁻¹	separation, cm⁻¹
15 191	
14 943	248
14 577	366
14 263	314
13 940	323
13 617	323
13 298	319
12 977	321
12 669	308

Table II. Far-Infrared Spectrum of [Pt(bpy)Cl₂] in the ν(Pt–Cl) Region (cm⁻¹)[a]

298 K	80 K
	303 vw
316 vs	318 vs
	333 w
341 vs	342 vs
	349 w

[a] Key: vs = very strong; w = weak; vw = very weak.

Table III. Classification of Normal Modes of a Square-Planar MX₄ Molecule in D_{4h} and SU(3)

D_{4h} designation[a]	type of vib[a]	V
$\nu_1(a_{1g})$	ν_s(M–X)	0
$\nu_2(b_{1g})$	δ(X–M–X)	2
$\nu_3(a_{2u})$	π	1
$\nu_4(b_{2g})$	ν_{as}(M–X)	2
$\nu_5(b_{2u})$	π	3
$\nu_6(e_u)$	ν_d(M–X)	1
$\nu_7(e_u)$	δ_d(X–M–X)	3

[a] See ref 22. Key: ν, stretch; δ, bend; π, out-of-plane bend; s, symmetric; as, antisymmetric; d, degenerate.

That portion of the far-infrared spectrum associated with the Pt–Cl stretching frequencies is reported in Table II at both 80 and 298 K.

Discussion

Table III lists the V quantum numbers for the seven normal vibrations of a square-planar MX₄ molecule.[22] Probably the best resolved luminescence spectrum of a square-planar complex in the literature is that by Patterson et al. of PtCl₄²⁻ in a Cs₂ZrCl₆ host lattice at 4 K, in which even the chlorine isotopic splitting is evident.[23,24] The electronic transition responsible for the luminescence of PtCl₄²⁻ may be represented[25] as ³F → ¹D, so that $\Delta L = 1$ and $\Delta S = 1$.

According to eq 1, then, the only vibrations which may enable the transition are those with $\Delta V = 1$, which means that either $\nu_3(a_{2u})$ or $\nu_6(e_u)$ must be associated with the ground electronic state, and that after the transition, the ground state will be distorted along one or both of these coordinates. Patterson's data show an average spacing between vibronic peaks of 326 cm⁻¹ for the most common [Pt³⁵Cl₃³⁷Cl]²⁻ isotopic composition. This is certainly well within the range expected

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for the a_{1g} mode, which has been observed in Raman spectra at frequencies between 328 and 335 cm⁻¹.[17,19-21] However, the spacing might also be appropriate to the $\nu_6(e_u)$ stretching frequency, which has been observed in IR spectra at 313–328 cm⁻¹.[18,19,21] A very careful study done recently by Adams and Berg[26] found ν_6 frequencies of 322 and 325 cm⁻¹ for the ammonium and potassium salts, respectively, which increased to 326 and 328 cm⁻¹ at 20 K. This evidence is certainly suggestive of an odd-mode structure but is far from conclusive since the corresponding data for $PtCl_4^{2-}$ in the Cs_2ZrCl_6 host lattice are not available.

We have found that the complex [Pt(bpy)Cl₂] at 12 K as an undoped powder also exhibits vibronic structure in luminescence. Though the resolution is far from that achieved by Patterson on $PtCl_4^{2-}$, it appears that it is the same $\nu(Pt–Cl)$ vibration which accounts for the band structure. The observed spacing of 320 cm⁻¹ can be clearly identified with the lower frequency Pt–Cl stretching mode.

In the [Pt(bpy)Cl₂] complex, which has approximately C_{2v} symmetry, the Pt–Cl stretch may occur symmetrically or antisymmetrically, with $V = 0$ and 1, respectively. Both are infrared active. If the analogy with $PtCl_4^{2-}$ can be constructed, then the higher of the two frequencies represents the symmetric stretching frequency, and thus the antisymmetric forms the basis for the electronic band structure. A Raman spectrum would be expected to shed some light on this assignment, but we were unable to obtain scattering using the 514-nm line of an argon ion laser (shorter wavelengths led to sample decomposition).

A substantive question with regard to the above analysis is whether d–d emission is observed in [Pt(bpy)Cl₂], as we have assumed, or π*–d emission. The question is not simply answered, but evidence for the d–d nature comes from (1) comparison with some other dichlorodiamines,[27] which have similar emission maxima, (2) a comparison with [Pt(bpy)₂]²⁺, which emits at higher energy (525 nm for the perchlorate salt[28] (even in [Pt(bpy)₂]²⁺, it is not clear that the emission is π*–d), and (3) the lifetime (18 μs at 77 K)[29] of [Pt(bpy)Cl₂], which is similar to those observed for other Pt(II) complexes with d–d emission.

In conclusion, the available evidence suggests that progressions in an antisymmetric ($V = 1$) stretching mode are responsible for the electronic band structure in the luminescence spectrum of $PtCl_4^{2-}$ and Pt(bpy)Cl₂, as predicted by the octupole selection rule of Hollebone[15] but is not yet conclusive. The present work should be taken as a stimulus to report infrared and Raman data, under as similar conditions as possible, in future vibronic (in particular, luminescence) studies of transition-metal complexes.

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Syntheses of Iron Carbonyl Trimethylsilanes: Preparations and Interconversions of cis-(CO)₄Fe[Si(CH₃)₃]₂, M⁺[(CO)₄FeSi(CH₃)₃]⁻, and trans-[-Fe(CO)₄Si(CH₃)₃]₂

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Reaction of petroleum ether slurries of M₂Fe(CO)₄ (M = Na, K) with (CH₃)₃SiBr results in ca. 50% yields of cis-(CO)₄Fe[Si(CH₃)₃]₂ (1). When K₂Fe(CO)₄ is reacted with (CH₃)₃SiBr for 0.5 h in THF, fair yields of K⁺[(CO)₄FeSi(CH₃)₃]⁻ (2a) are obtained. Reaction of (CO)₄Fe(H)Si(CH₃)₃ with KH and NaH affords 2a (90%) and Na⁺[(CO)₄FeSi(CH₃)₃]⁻ (2c; 68%), respectively. Both 2a and 2c are oxidized by C₇H₇⁺PF₆⁻ to the labile binuclear complex trans-[-Fe(CO)₄Si(CH₃)₃]₂ (3). Complex 3 can be independently generated from 1 and benzaldehyde and is reduced by Na/Hg to 2c. Other reactions and interconversions of these silanes are described. Some earlier unsuccessful attempts to prepare 1 by related routes are discussed.

Introduction

(Trimethylsilyl)- and (trialkylsilyl)iron carbonyl complexes are finding increasing application in organic and organometallic synthesis.[1-3] Consequently, we have sought to synthesize new complexes in this series that may have useful properties. In this paper, we describe syntheses and interconversions of the iron trimethylsilanes cis-(CO)₄Fe[Si(CH₃)₃]₂ (1), M⁺[(CO)₄FeSi(CH₃)₃]⁻ (M⁺: K⁺, 2a; [(C₆H₅)₃P]₂N⁺, 2b; Na⁺, 2c; [(C₂H₅)₂N]₃S⁺, 2d), and trans-[Fe(CO)₄Si(CH₃)₃]₂ (3). Although 1 is a known compound, the preparation herein represents a distinct improvement of the literature procedure[4] and is of interest in view of the history of this molecule (vide infra).[5-7] A portion of this

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