Contribution from the Department of Chemistry,
University of Western Ontario, London, Ontario, Canada N6A 5B7

Electronic Structure of (β-Diketonato)trimethylplatinum(IV) Complexes from UV Photoelectron Spectra and SCF-MS-Xα Calculations

Dong-Sheng Yang, G. Michael Bancroft,* and Richard J. Puddephatt*

Received May 31, 1989

The UV photoelectron spectra of the (β-diketonato)trimethylplatinum(IV) complexes $[PtMe_3(acac)]_2$ (acac = acetylacetonate), $[PtMe_3(tfa)H_2O]$ (tfa = trifluoroacetylacetonate), $[PtMe_3(hfa)H_2O]$ (hfa = hexafluoroacetylacetonate), and $[PtMe_3(tfa)Me_2S]$ are reported. The valence orbitals responsible for the ionizations have been assigned by using the MS-Xα result for the model compound $[PtMe_3(HC(O)CHCOH)]$ and the ionization shifts from the ligand substitutions. The valence molecular orbitals fall in the order of increasing binding energy $\pi_3 < n_- <$ Pt-$n_+ <$ Pt 5d, Pt-Me in the complexes $[PtMe_3(acac)]$, $[PtMe_3(tfa)H_2O]$, and $[PtMe_3(hfa)H_2O]$ and in the order Pt-S $< \pi_3 < n_- <$ Pt-$n_+ <$ Pt 5d in the compound $[PtMe_3(tfa)Me_2S]$. Both photoelectron spectra and the MS-Xα calculation indicate that the Pt 5d electrons are extensively delocalized by interaction with the coordinated ligands.

Introduction

Since the discovery of the compound $[Me_3Pt(acac)]_2$ (acac = acetylacetonate) in 1928,[1] the β-diketonate complexes of trimethylplatinum(IV) have been extensively investigated. These studies include chemical reactions,[2] thermoanalysis,[3] X-ray diffraction,[3-5] NMR spectroscopy,[6-9] and IR and UV spectroscopy and mass spectrometry.[8,10] The extensive studies on this type of complex appear to be due to their theoretical relevance to the nature of the metal-ligand bond and the general features of adduct formation. However, there has not been any experimental determination of the relative ionization energies of the valence orbitals, in particular the σ Pt-ligand and Pt 5d orbitals in these molecules. Since UV photoelectron spectroscopy is the most direct and powerful technique for the elucidation of the electronic structure and bonding in classic coordination and organometallic compounds of transition elements,[11-14] we have undertaken a detailed He I and He II photoelectron spectroscopic study of complexes $[Me_3Pt(acac)]_2$ (which we propose is monomeric at higher temperatures in the gas phase), $[Me_3Pt(tfa)H_2O]$ (tfa = trifluoroacetylacetonate), $[Me_3Pt(tfa)Me_2S]$, and $[Me_3Pt(hfa)H_2O]$ (hfa = hexafluoroacetylacetonate). To aid in the assignments, we have also carried out a SCF-MS-Xα calculation on the model molecule $[Me_3Pt(HC(O)CHCOH)]$. The SCF-MS-Xα method has enjoyed great success in helping to interpret the photoelectron spectra of organometallic molecules.[15-24]

Experimental Section

Synthesis and Characterization. Melting points were measured in capillary tubes without correction. The ^1H NMR and ^{19}F NMR spectra were recorded on a Varian XL-200 and a Varian XL-300 spectrometer, respectively. Mass spectra were obtained by electron impact on a Finigan MAT 8230 spectrometer employing an ionization voltage of 70 eV. Elemental analysis was obtained from Guelph Chemical Laboratories, Ltd.

$[PtMe_3(acac)]_2$ was prepared by the literature method[16] and identified by the melting point (200 °C dec)[25] and ^1H NMR spectrum.[26] The mass spectrum (parent ion m/z 399) showed that this compound is a monomer under these conditions, and our spectra below also show that it is a monomer at higher temperatures.

$[PtMe_3(tfa)Me_2S]$. To a suspension $[Pt_2Me_8(\mu\text{-}SMe_2)_2]$[27] (0.260 g, 0.41 mmol) in dry ether (15 mL) was added trifluoroacetylacetone (0.15 mL, 1.20 mmol). The yellow-orange solution was stirred at room temperature for 5 h. The solvent was evaporated under reduced pressure, and the excess free ligand was removed by heating up to 50 °C (water bath) for 3 h. The oily residue was then sublimed at 80 °C to give a yellow liquid (0.16 g, 42.9% yield). ^1H NMR ($CDCl_3$): δ 0.98 (s, ^2J(Pt-H) = 74.1 Hz, Pt-CH_3), 2.05 (s, CH_3, tfa), 2.16 (s, Me_2S), 5.57 (s, CH, tfa). ^{19}F NMR ($CDCl_3$): δ -75.6 (s, tfa). Molecular weight: 455 (mass spectrum). Anal. Calcd for $C_{10}H_{19}O_2F_3SPt$: C, 26.37; H, 4.18. Found: C, 25.95; H, 4.19.

$[PtMe_3(hfa)H_2O]$. $[Me_3PtI]_4$ (0.300 g, 0.82 mmol) was dissolved in warm, glass-distilled benzene (20 mL). Tl(hfa) (0.350 g, 0.85 mmol) in 95% ethanol (5 mL) was then added to the orange benzene solution. The mixture was stirred at 70 °C under reflux for 3 h. The thallous iodide that separated was removed, and the filtrate was evaporated to dryness. The dry residue was extracted with ether (50 mL), and the extract was evaporated to dryness again. The product was recrystallized from hot hexane (1 mL) and additionally purified by sublimation to give a yellow solid (0.23 g, 60.6% yield). Mp: 105-107 °C (dec pt 125 °C). ^1H NMR ($CDCl_3$): δ 1.22 (s, ^2J(Pt-H) = 78.7 Hz, Pt-CH_3), 2.09 (s, H_2O), 5.94 (s, CH, hfa). ^{19}F NMR ($CDCl_3$): δ -76.1 (s, hfa). Molecular weight: 465 (mass spectrum). Anal. Calcd for $C_8H_{12}O_3F_6Pt$: C, 20.65; H, 2.58. Found: C, 19.51; H, 2.05.

Preparation of $[PtMe_3(tfa)H_2O]$ followed the procedure for preparing $[PtMe_3(hfa)H_2O]$. A white solid product was obtained. Mp: 101 °C. ^1H NMR ($CDCl_3$): δ 1.17 (s, ^2J(Pt-H) = 77.8 Hz, Pt-CH_3), 2.02 (s, CH_3, tfa), 2.08 (s, H_2O), 5.61 (s, CH, tfa). ^{19}F NMR ($CDCl_3$): δ -75.3 (s, tfa). Molecular weight: 411 (mass spectrum).

Photoelectron Spectroscopy. UV photoelectron spectra were recorded on a McPherson ESCA-36 photoelectron spectrometer equipped with a hollow-cathode UV He lamp.[28] The spectra of the compounds

---

(1) Menzies, R. C. *J. Chem. Soc.* **1928**, 565.
(2) Kite, K.; Truter, M. R. *J. Chem. Soc. A* **1968**, 934.
(3) Zharkova, G. I.; Igumenov, I. K.; Zemskov, S. V.; Durasov, V. B. *Koord. Khim.* **1979**, *5*, 1073.
(4) Swallow, A. G.; Truter, M. R. *Proc. R. Soc. London A* **1960**, *254*, 205.
(5) Hazell, A. C.; Truter, M. R. *Proc. R. Soc. London A* **1960**, *254*, 218.
(6) Hall, J. R.; Swile, G. A. *J. Organomet. Chem.* **1970**, *21*, 237.
(7) Clegg, D. E.; Hall, J. R.; Ham, N. S. *Aust. J. Chem.* **1970**, *23*, 1981.
(8) Hall, J. R.; Swile, G. A. *J. Organomet. Chem.* **1973**, *47*, 195.
(9) Ham, N. S.; Hall, J. R.; Swile, G. A. *Aust. J. Chem.* **1975**, *28*, 759.
(10) Zharkova, G. I.; Igumenov, I. K.; Zemskov, S. V. *Koord. Khim.* **1979**, *5*, 586.
(11) Green, J. C. *Struct. Bonding (Berlin)* **1981**, *43*, 37.
(12) Cowley, A. H. *Prog. Inorg. Chem.* **1979**, *26*, 45.
(13) Solomon, E. I. *Comments Inorg. Chem.* **1984**, *3*, 227.
(14) Lichtenberger, D. L.; Kellogg, G. E. *Acc. Chem. Res.* **1987**, *20*, 379.
(15) Bancroft, G. M.; Chan, T. C. S.; Puddephatt, R. J. *Inorg. Chem.* **1983**, *22*, 2133.
(16) Bice, J. E.; Bancroft, G. M.; Coatsworth, L. L. *Inorg. Chem.* **1986**, *25*, 2181.
(17) Yang, D. S.; Bancroft, G. M.; Bozek, J. D.; Puddephatt, R. J.; Tse, J. S. *Inorg. Chem.* **1989**, *28*, 1.
(18) Yang, D. S.; Bancroft, G. M.; Puddephatt, R. J.; Tse, J. S. *Inorg. Chem.*, in press.
(19) Yang, D. S.; Bancroft, G. M.; Puddephatt, R. J.; Tse, J. S. *Inorg. Chem.*, in press.
(20) Bursten, B. E.; Cotton, F. A.; Stanley, G. G. *Isr. J. Chem.* **1980**, *19*, 132.
(21) Bursten, B. E.; Casarin, M.; Dibella, S.; Faug, A.; Fragala, I. L. *Inorg. Chem.* **1985**, *24*, 1241.
(22) Cotton, F. A.; Stanley, G. G.; Cowley, A. H.; Lattman, M. *Organometallics* **1988**, *7*, 835.
(23) Guimon, G.; Pfister-Guillouzo, G.; Chaudret, B.; Poilblanc, R. *J. Chem. Soc., Dalton Trans.* **1985**, 43.
(24) Elbel, S.; Grodzicki, M.; Pille, L.; Ünger, G. *J. Mol. Struct.* **1988**, *175*, 441.
(25) Menzies, R. C. *J. Chem. Soc.* **1928**, 565.
(26) Kite, K.; Smith, J. A. S.; Wilkins, E. J. *J. Chem. Soc. A* **1966**, 1744.
(27) Lashanizadehgan, M.; Rashidi, M.; Hux, J. H.; Puddephatt, R. J. *J. Organomet. Chem.* **1984**, *269*, 317.

0020-1669/90/1329-2118$02.50/0 © 1990 American Chemical Society

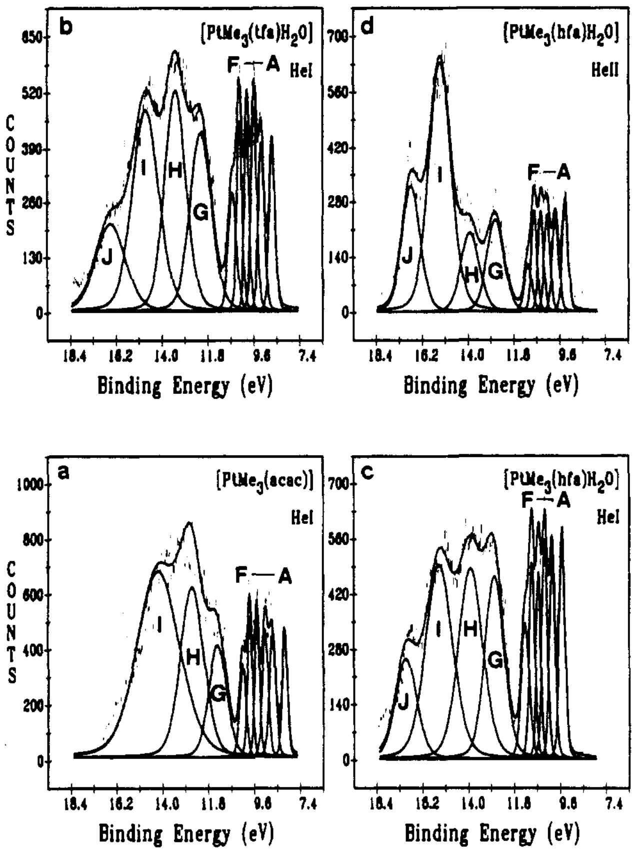

Figure 1. He I spectra of (a) [$PtMe_3(acac)$] (Ar calibration) and (b) [$PtMe_3(tfa)H_2O$] and (c) He I and (d) He II spectra of [$PtMe_3(hfa)H_2O$].

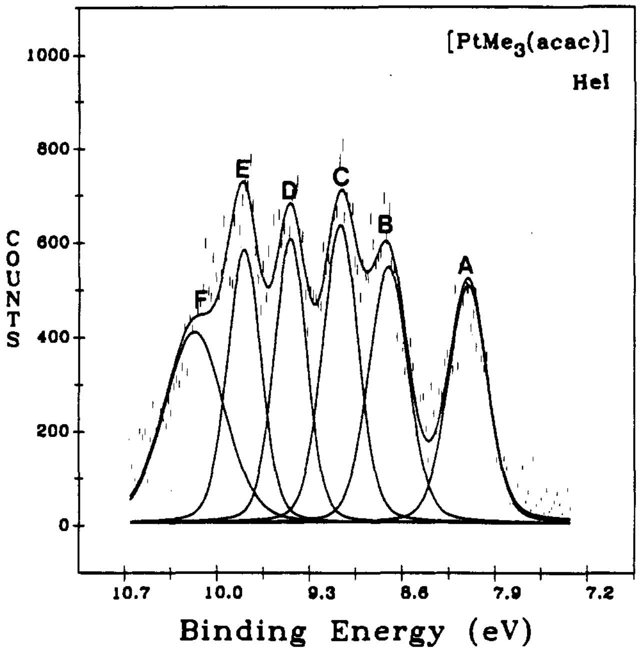

Figure 2. Expansion of the low-energy region of the He I spectrum of [$PtMe_3(acac)$].

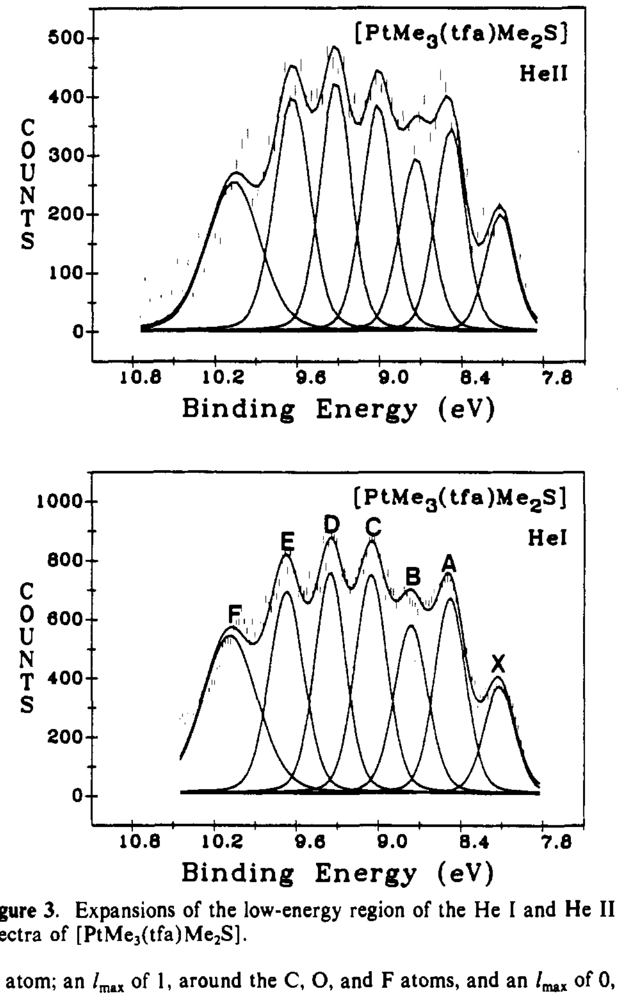

Figure 3. Expansions of the low-energy region of the He I and He II spectra of [$PtMe_3(tfa)Me_2S$].

[$PtMe_3(tfa)H_2O$], [$PtMe_3(tfa)Me_2S$], and [$PtMe_3(hfa)H_3O$] were obtained at temperatures of 80–90 °C. For the compound [$PtMe_3(acac)$]$_2$, we started collecting the spectrum at 90 °C and ended at 185 °C; the unique, reproducible He I spectrum could only be obtained above 125 °C. This strongly indicated that the compound was a monomer above 125 °C. Its He II spectrum was poor due to the low vapor pressure. The argon $^2P_{3/2}$ ionization at 15.76 eV was used as internal calibration during data acquisition. The resolution (fwhm of Ar $^2P_{3/2}$ ionization) was less than 0.027 and 0.036 eV for the He I and He II sources, respectively. Spectra were fitted to Lorentzian–Gaussian line shapes with the use of an iterative procedure,[29] with reproducibility of the vertical ionization energy (IE) of ±0.02 eV. The relative band areas are reproducible to about 10% in the He I spectra and about 15% in the He II spectra. The band area ratios from the He I and He II spectra were corrected for the electron analyzer transmission energy by dividing by the kinetic energy of the band.

Computational Details. The calculations were performed by using the relativistic version of the Xα scattered-wave method,[30] in which the relativistic radial-wave functions around the Pt atom have been employed. The exchange α parameters used in each atomic region were from Schwarz's tabulation,[31] except for hydrogen, for which 0.77725 was used.[32] For the extramolecular and intersphere regions, a weighted average of the atomic α's, 0.74852, was employed, the weight being the number of valence electrons in neutral atoms. Overlapping-sphere radii were used.[33,34] An l_{max} of 3 was used around the outer sphere and the Pt atom; an l_{max} of 1, around the C, O, and F atoms, and an l_{max} of 0, around the H atoms. The geometry was based on the X-ray data for the compound [$PtMe_3(C_3H_7C(O)CHCOC_3H_7)$]$_2$ and was optimized to have C_s symmetry.[35]

---

(28) Coatsworth, L. L.; Bancroft, G. M.; Creber, D. K.; Lazier, R. J. D.; Jacobs, P. W. P. *J. Electron. Spectrosc. Relat. Phenom.* **1978**, *13*, 395.

(29) Bancroft, G. M.; Adams, J.; Coatsworth, L. L.; Bennewitz, C. D.; Brown, J. D.; Westwood, W. D. *Anal. Chem.* **1975**, *47*, 586.

(30) Johnson, K. H. *Adv. Quantum Chem.* **1973**, *7*, 147. Herman, F.; Willians, A. R.; Johnson, K. H. *J. Chem. Phys.* **1974**, *61*, 3508. Case, D. A.; Yang, C. Y. *Int. J. Quantum Chem.* **1980**, *18*, 1091. Cook, M.; Case, D. A. *QCPE* **1982**, *14*, 465.

(31) Schwarz, K. *Phys. Rev. B* **1972**, *5*, 2466; *Theor. Chim. Acta* **1974**, *34*, 225.

(32) Slater, J. C. *Int. J. Quantum Chem.* **1973**, *7s*, 533.

(33) Norman, J. G., Jr. *J. Chem. Phys.* **1974**, *61*, 4630; *Mol. Phys.* **1976**, *31*, 1191.

(34) Atomic and outer-sphere radii (bohrs): outer, 7.4777; Pt, 2.6577; C, 1.6794; O, 1.5547; H, 1.2105.

(35) Pt–C_{Me} = 2.03 Å, Pt–O = 2.15 Å, O–C = 1.23 Å, C–C = 1.46 Å, C–Pt–C = 88.6°, O–Pt–O = 88.9°, Pt–O–C = 124.4°, O–C–C = 128.0°, C–C–C = 122.0°, C–H = 1.10 Å, H–C–H = 109.5°: Swallow, A. G.; Truter, M. R. *Proc. R. Soc. London* **1960**, *254A*, 205.

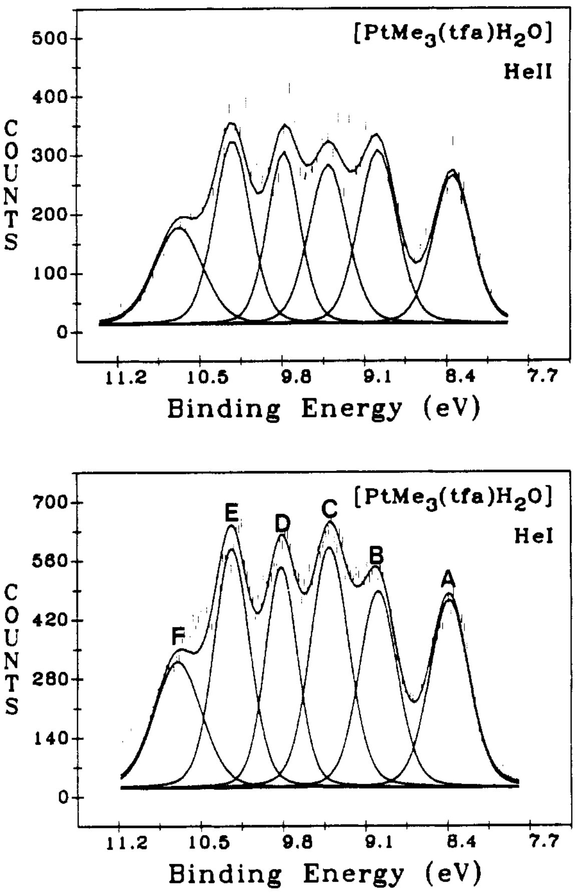

Figure 4. Expansions of the low-energy region of the He I and He II spectra of [$PtMe_3(tfa)H_2O$)].

Table I. Vertical Ionization Energies, He II/He I Band Area Ratios, and Assignments of the Photoelectron Spectra of (β-Diketonato)trimethylplatinum(IV) Complexes

compd	band	IE, eV	He II/He I area ratio[a]	assgnt
[$PtMe_3(acac)$]	A	8.10		π_3
	B	8.68		n_-
	C	9.05		d_{z^2}, n_+
	D	9.45		d_{xz}, Me
	E	9.81		d_{xy}
	F	10.19		d_{z^2}, Me
[$PtMe_3(tfa)Me_2S$]	X	8.30	1.00	$d_{z^2-y^2}$, Me_2S
	A	8.65	0.95	π_3
	B	8.95	0.96	n_-
	C	9.25	0.96	d_{z^2}, n^+
	D	9.53	1.07	d_{xz}, Me
	E	9.87	1.13	d_{xy}
	F	10.29	0.96	d_{z^2}, Me
[$PtMe_3(tfa)H_2O$]	A	8.67	1.00	π_3
	B	9.20	1.05	n_-
	C	9.55	0.85	d_{z^2}, n^+
	D	9.90	1.01	d_{xz}, Me
	E	10.25	1.00	d_{xy}
	F	10.63	1.01	d_{z^2}, Me
[$PtMe_3(hfa)H_2O$]	A	9.16	1.00	π_3
	B	9.66	1.01	n_-
	C	10.02	0.83	d_{z^2}, n_+
	D	10.32	0.97	d_{xz}, Me
	E	10.66	0.94	d_{xy}
	F	11.04	0.83	d_{z^2}, Me

[a] Referenced to band A.

Results and Discussion

General Features of the Spectra. UV photoelectron spectra are presented in Figures 1–5. The curve-fitting analysis for the valence bands in the low ionization energy region are reported in Table I.

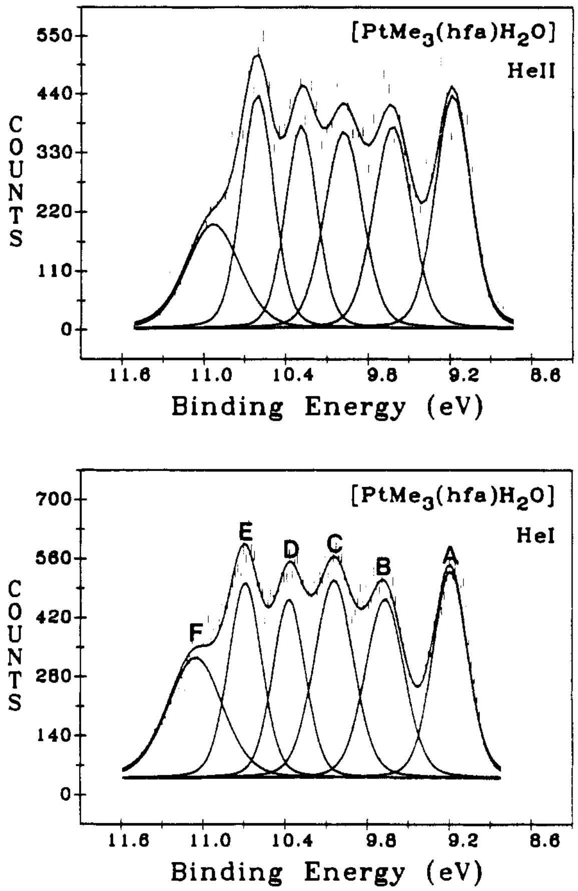

Figure 5. Expansions of the low-energy region of the He I and He II spectra of [$PtMe_3(hfa)H_2O$)].

Table II. Ionization Energy Shift of Each Band in (β-Diketonato)trimethylplatinum(IV) Complexes

	A	B	C	D	E	F
[$PtMe_3(tfa)Me_2S$]–[$PtMe_3(acac)$]	0.55	0.27	0.20	0.08	0.06	0.10
[$PtMe_3(hfa)H_2O$]–[$PtMe_3(acac)$]	1.06	0.98	0.97	0.87	0.85	0.84
[$PtMe_3(tfa)H_2O$]–[$PtMe_3(tfa)Me_2S$]	0.02	0.25	0.30	0.37	0.38	0.35

In the region >11 eV, the spectra show broad envelopes, and a minimum number of bands to adequately simulate this region has been fitted (Figure 1). Band J (~17 eV) in Figure 1b–d is absent in Figure 1a. This band is assigned to the ionizations of C–F σ orbitals.[36] Band I (~15 eV) shows a great He II intensity enhancement (Figure 1d), and thus it is associated with fluorine 2p lone-pair ionizations.[37,38] Bands G and H show reduced He II intensities, and they probably arise from a large number of non-fluorine ligand orbital ionizations, as well as low-energy Pt–Me σ orbitals. These ionizations will not be discussed further due to the featureless band structures.

In the region <11 eV, ionization bands are narrow and well resolved compared to those at higher ionization energy. Six bands are present in all spectra (Figure 2, 4, and 5) except for the spectrum of the compound [$PtMe_3(tfa)Me_2S$] in which an additional band (X) is displayed (Figure 3). It is evident that all of the bands (A–F) in this region are shifted to higher ionization energy from the compound [$PtMe_3(acac)$] to the compounds [$PtMe_3(tfa)H_2O$] and [$PtMe_3(hfa)H_2O$]. For example, three bands (D–F) are shifted by about 0.85 eV from [$PtMe_3(acac)$]

---

(36) Drake, J. E.; Eujen, R.; Gorzelska, K. *Inorg. Chem.* **1982**, *21*, 1784.

(37) Coleman, A. W.; Green, J. C.; Hayes, A. J.; Seddon, E. A.; Lloyd, D. R.; Nowa, Y. *J. Chem. Soc., Dalton Trans.* **1979**, 1057.

(38) Cauletti, C.; Clark, J. P.; Green, J. C.; Jackson, S. E.; Fragala, I. L.; Ciliberto, E.; Coleman, A. W. *J. Electron Spectrosc. Relat. Phenom.* **1980**, *18*, 61.

Table III. MS–Xα Results for [$PtMe_3(HC(O)CHCOH)$] Upper Valence Orbitals

MO	energy, eV^b		charge distribution, %^{a}														dominant character
			Pt														
			s	p	d	C_1	C_2	O	C_3	C_4	H_1	H_2	H_3	int	out	
6a′	5.85	8.40			1			16	8	40				33	2	π_3
3a″	7.65	10.08		6	1		6	47	6	10			6	18		n_-
5a′	7.93	10.21		4	23	1	11	33	1	7	2	2	2	13	1	d_{z^2}, n_+
4a′	8.50	10.67	5		46	9	7	4	1	1	9	2		15	1	d_{xz}, Me
2a″	8.73	10.91			76	3	3	1	1		4	4		8		d_{xy}
3a′	8.82	10.96	7	2	48	5	18	1	1		2	4		11	1	d_{z^2}, Me
2a′	9.47	11.73	4		45	3	4	14	2	7		5	3	12	1	d_{xz}, π_3
1a″	10.75	12.95		1	44		24	6	6	4		7		8		d_{yz}, Me
1a′	11.35	13.54	1	1	46	21	3	7	4	2	5	1	1	8		$d_{x^2-y^2}$, Me

[a] Atoms C_1 and H_1 are the carbon and hydrogen atoms of the axial methyl group (see Figure 6). Atoms C_2 and H_2 are the carbon and hydrogen atoms of the two equatorial methyl groups. Atom C_3 represents the two β-carbons of the model acac ligand, and atom C_4 represents the central carbon atom. H_3 represents the three hydrogen atoms of the model acac ligand. [b] The energies in the second column are the molecular orbital energies of the ground state, and those in the third column are the transition-state energies.

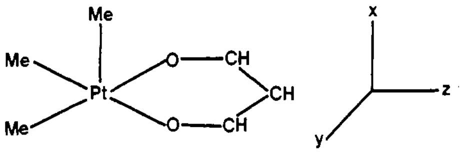

Figure 6. Geometry adopted for the model compound [$PtMe_3(HC(O)CHCOH)$] in the MS–Xα calculation.

to [$PtMe_3(hfa)H_2O$] with bands A–C shifted to a larger extent (1 eV) (Table II). Similar features have been observed for other (β-diketonato)metal complexes and explained in terms of the fluorine inductive effect.[36,39–41] It is also interesting to note that bands D–F of the compound [$PtMe_3(tfa)Me_2S$] have almost the same energies as the corresponding bands of the compound [$PtMe_3(acac)$] (Table I), implying that the fluorine effect on these bands (D–F) is almost cancelled by the strong σ donor Me_2S replacing the weak donor H_2O. Finally, all bands (A–F) show no significant differences in He II/He I area ratios (Table I), as observed in square-planar platinum(II) complexes.[17–19] These bands (A–F) will receive primary attention in the following discussion.

Molecular Orbital Calculation. (Acetylacetonato)trimethylplatinum(IV) is known to be binuclear in the solid state, with each platinum being octahedrally coordinated to three methyl groups in a cis configuration, to two oxygens of one β-diketone, and to the central carbon atom of the other diketone.[4,5] In the gas phase at temperatures from 125 to 180 °C, however, this complex is a monomer, as shown by our photoelectron measurements at variable temperatures (see Experimental Section). In the monomeric form of this compound, the bond between platinum and the central carbon is broken and the platinum atom is five-coordinate. Therefore, the molecular orbital calculation was performed on this monomer structure as shown in Figure 6. Although the molecules [$PtMe_3(tfa)H_2O$] and [$PtMe_3(hfa)H_2O$] have octahedral structures with H_2O on the sixth coordinate site of the platinum atom, we believe that their valence electronic structures are similar to that of the parent (acetylacetonato)platinum molecule, as evidenced by their similar photoelectron spectra. The valence electronic structure of the molecule [$PtMe_3(hfa)Me_2S$] is slightly different, as revealed by the additional band (X) in its photoelectron spectrum (Figure 3), but the origin of this additional peak is readily rationalized without a theoretical calculation (see the section on spectral assignment and interpretation).

The molecular orbital results for the nine valence orbitals of the model compound [$PtMe_3(HC(O)CHCOH)$] are reported in Table III. These nine MO's are all related mainly to the Pt 5d orbitals and ligand lone pairs (as well as the outermost π (π_3) orbital of the acac ligand). To discuss these data, it is helpful to mention first the relevant upper valence orbitals of the free acac ligand that are mainly responsible for the bonding with the central Pt atom. These are the combinations of two in-plane oxygen 2p lone pairs n_+ and n_- (a′ and a″ in C_s, respectively) and the π_3 (a′) orbital formed from the symmetric combination of two π_{CO} orbitals and the pπ (p_x in the coordinate system of Figure 6) orbital of the unique central carbon atom.[42] The energy ordering of the above MO's was previously calculated as $\pi_3 > n_- > n_+$.[42] The symmetric combination n_+ orbital interacts strongly with the hydrogen 1s orbital to form an O–H bond in the enol form of the free acacH ligand.[42] In the molecule [$PtMe_3(acac)$], the hydrogen of the ligand acacH is replaced by the platinum atom and thus the n_+ orbital is expected to be the major source for the Pt–O σ interaction.

The highest molecular orbital (HOMO), 6a′, is essentially a π_3 contribution of the ligand acac, with the electrons largely on the unique central carbon atom (Table III). The 6a′ orbital is followed by the 3a″ MO with predominant n_- character of the acac ligand and only a small Pt contribution. The 5a′ orbital has a heavy σ mixing between the Pt 5d (mainly $5d_{z^2}$) and the n_+ orbital, as expected by the above qualitative considerations. Although the Pt $5d_{z^2-y^2}$ and $5d_{xz}$ orbitals also have the a′ representation, they are not in the same plane as that of the n_+ orbital. Therefore we assume no significant interactions with the n_+ orbital. Similar assumptions are followed below. Next, there are six MO's that all contain largely Pt 5d character. Three of them are σ-type orbitals and the other three are π-type orbitals. Among the σ MO's are the 3a′, 1a″, and 1a′ orbitals. The 3a′ MO consists of the Pt $5d_{z^2}$ orbital mixed with the symmetric combination of the two carbon lone pairs of the equatorial methyl groups. The 1a″ and 1a′ MO's, located at low energy, are the strong Pt–Me σ-bonding orbitals. The 1a″ orbital is the Pt $5d_{yz}$ orbital mixed with the antisymmetric combination of the carbon lone pairs of the two equatorial methyl groups, while the 1a′ orbital is the Pt $5d_{x^2-y^2}$ orbital mixed with the carbon lone pair of the axial methyl group. Three π-type MO's are the 4a′, 2a″, and 2a′ orbitals. The 4a′ and 2a′ MO's have much Pt $5d_{xz}$ character, mixed with a C–H σ orbital of the axial methyl group and the π_3 orbital of the acac ligand, respectively, while the 2a″ orbital has essentially Pt $5d_{xy}$ character.

It is noted from this theoretical result that there is extensive delocalization of the Pt 5d electrons to the ligand orbitals in the (β-diketonato)trimethylplatinum(IV) molecules. As a result, simple formal oxidation state and d-electron-count descriptions are not suitable in these cases. For example, the simple formal state and d-electron count give six Pt 5d electrons in these molecules, but only the molecular orbital 2a″ contains the "pure" Pt $5d_{xy}$ electrons. Similar features in the cyclopentadienyl d^8 metal complexes have also been discussed by Lichtenberger et al.[14]

Spectral Assignment and Interpretation. Since the spectra of the four compounds are very similar (see Figures 2–5), the dis-

---

(39) Lloyd, D. R. *J. Chem. Soc. D* **1970**, 868. Evans, S.; Hamnett, H.; Orchard, A. F. *J. Coord. Chem.* **1972**, *2*, 57.

(40) Cauletti, C.; Furlani, C. *J. Electron. Spectrosc. Relat. Phenom.* **1975**, *6*, 465.

(41) van Dam, H.; Terpstra, A.; Stufkens, D. J.; Oskam, A. *Inorg. Chem.* **1980**, *19*, 3448.

cussion that follows is applicable to all cases. The additional band (X) (Figure 3) of the compound [PtMe$_3$(tfa)Me$_2$S] will be assigned separately in the course of the discussion. For transition-metal complexes, it is often possible to use the He I and He II intensity difference to aid the spectral assignment, since d orbitals frequently have a larger relative photoionization cross section for He II radiation. However, as the data in Table I indicate, the low-energy bands in the photoelectron spectra give very similar He II/He I band area ratios and so this technique is not useful for these (β-diketonato)trimethylplatinum(IV) complexes, as for square-planar platinum(II) complexes.[17-19] Therefore, the spectra will be assigned by using the ionization energy shifts and the MS–Xα result for the model compound [PtMe$_3$(HC(O)CHCOH)].

Regarding the ionization energy shifts (Table II), we naturally expect that the ionizations of the β-diketonate ligand orbitals will have larger energy shifts than the Pt atom and Pt–Me orbitals with fluorine substitutions in the β-diketonate ligands. In contrast, we expect that the ligand-based orbitals will have smaller shifts than the Pt 5d and Pt–Me orbitals between the compounds [PtMe$_3$(tfa)H$_2$O] and [PtMe$_3$(tfa)Me$_2$S]. The energy shifts for these compounds are summarized in Table II. It is clear from Table II that band A has the largest energy shift from the parent acac compound to the fluorinated compounds, but little shift from the compound [PtMe$_3$(tfa)Me$_2$S] to [PtMe$_3$(tfa)H$_2$O]. This is strong evidence for band A arising from the π_3 ionization of the β-diketonate ligand, remembering that the IE ordering of the outermost orbitals in the free β-diketones is $\pi_3 < n_- < n_+$.[42] This assignment, which is based on the experimental observations, is in excellent agreement with the MS–Xα prediction in which the HOMO is calculated to be the π_3 orbital (see Table III). The π_3 orbital also gives rise to the lowest IE band in the compound [Pt(acac)$_2$].[43]

Bands D–F, on the other hand, show the least energy shifts with fluorine substitution (Table II) of all the bands in the low-IE region. This indicates that the three bands (D–F) contain largely Pt 5d character. Assuming that each ionization band corresponds to a single MO, the three bands D–F are assigned to the MO's 4a′ (d$_{xz}$, Me$_{ax}$)), 2a″ (d$_{xy}$), and 3a′ (d$_{z^2}$, Me$_{eq}$), respectively, for which predominant Pt 5d contributions are calculated (see Table III). The near degeneracy of the MO's 2a″ and 3a′, as predicted by the MS–Xα calculation (Table III), is also in accord with the poorer resolution of bands E and F, compared to other bands (A–D) (see Figures 2–5).

The ionization energy shifts of bands B and C are greater than those of bands D–F, but less than that of band A, upon fluorine substitution (see Table II). On the basis of the same argument as above, this is an indication that bands B and C must contain ionizations arising from the β-diketonate ligand orbitals as well as from the Pt atom orbitals. The MS–Xα calculation indeed predicts that the second and third highest occupied MO's (3a″ and 5a′) consist of the β-diketonate ligand orbitals (n$_-$ and n$_+$ respectively) mixed with some Pt character, especially a heavy mixing of the Pt 5d$_{z^2}$ orbital in the MO 5a′ (see Table III). The assignments for bands B and C are shown in Table I, in which only major contributions are indicated.

Finally, there is an additional band (X) in the spectrum of the compound [PtMe$_3$(tfa)Me$_2$S] (see Figure 3). This band has an ionization energy of 8.3 eV, which is similar to the lone-pair ionization energy (8.7 eV) of the free Me$_2$S.[44] The slightly lower IE of band X than of the lone pair of the free Me$_2$S might imply the Pt 5d$_{x^2-y^2}$ orbital being mixed with the lone-pair electrons in an antibonding σ manner, as indicated by the similar He I and He II intensities, since previous studies have provided evidence that, compared to carbon and oxygen 2p AO's, sulfur 3p AO's have lower photoionization cross sections for He II than for He I radiation.[45,46] Therefore, band X is assigned to the ionization of the Pt–S σ^* orbital.

Conclusions

The ionization energy of the first six valence MO's falls in the order π_3 < n$_-$ < Pt–n$_+$ < Pt 5d, Pt–Me in the complexes [PtMe$_3$(acac)], [PtMe$_3$(tfa)H$_2$O], and [PtMe$_3$(hfa)H$_2$O], while the ionization energy of the first seven valence MO's in the compound [PtMe$_3$(tfa)Me$_2$S] falls in the order Pt–Me$_2$S < π_3 < n$_-$ < Pt–n$_+$ < Pt 5d. There is strong interaction between the platinum 5d orbitals with both the β-diketonate n$_+$ and the methyl σ orbitals.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for financial support.

---

(42) Evans, S.; Hamnett, H.; Orchard, A. F.; Lloyd, D. R. *Faraday Discuss. Chem. Soc.* **1972**, *54*, 227.

(43) Bella, S. D.; Fragalà, I.; Granozzi, G. *Inorg. Chem.* **1986**, *25*, 3997.

(44) Kimura, K.; Katsumata, S.; Achiba, Y.; Yamazki, T.; Iwata, S. *Handbook of He I Photoelectron Spectra of Fundamental Organic Molecules*; Japan Scientific Societies Press: Tokyo, 1981; p 126.

(45) Schweig, A.; Thiel, W. *Mol. Phys.* **1974**, *27*, 265.

(46) Granozzi, G.; Vittadini, A.; Sindellari, L.; Ajò, D. *Inorg. Chem.* **1984**, *23*, 702.