Inorg. Chem. **2001,** *40,* 3351−3354

Structure and Electron Affinity of Platinum Fluorides

Ralf Wesendrup and Peter Schwerdtfeger*

Department of Chemistry, The University of Auckland, Private Bag 92019, Auckland, New Zealand

Received February 9, 2001

The structure, stability, and electron affinity of the even numbered molecular platinum fluorides PtF_{2n} ($n = 1-4$) were studied by scalar relativistic density functional and coupled cluster methods. The di, tetra, and hexafluorides possess triplet ground states, while PtF_8 is a singlet. Formation of the latter from PtF_6 and F_2 is found to be endothermic. Differences between adiabiatic and vertical electron affinities are only significant for PtF_2.

Introduction

The preparation of high oxidation state compounds is still a very active area of research.[1] The maximum oxidation state is +8, as known for the oxides OsO_4, RuO_4, and XeO_4, but even higher oxidation states may be feasible, as recently proposed by Pyykkö for uranium oxides.[2] For the fluorides the maximum oxidation state seems to be +7, as this is the case for IF_7, ReF_7, or OsF_7.[3−5] These compounds are, however, very unstable and represent powerful fluorination agents.

Although OsF_8 was recently predicted to be a metastable compound,[6] fluorides in the oxidation state +8 are unknown, with the exception of mixed oxofluorides such as XeO_2F_4.[7] Theoretically, relativistic effects could stabilize high oxidation states for the heavy transition elements.[8] The relativistic stabilization of the valence 6s orbital and destabilization of the 5d diminishes the 5d−6s gap especially for the elements around Au, i.e., Hg and Pt.[9] This has been demonstrated for AuF_6^- and for the proposed high oxidation state compound of mercury, HgF_4.[10−13]

The highest oxidation state for platinum is +6,[14] and PtO_3 has been investigated recently by Andrews and co-workers using matrix infrared spectroscopy.[15] In the gas phase PtO and PtO_3 are open-shell species,[15−17] while the electronic ground states of isolated PtF_2 and PtF_4 are yet unknown. The thermochemistry of the di, tetra, and hexafluoride of platinum has been studied by means of mass spectroscopy,[18−21] but with the exception of PtF_6, their actual gas phase structures have yet to be established.[22] PtF_6 is also one of the molecules with the highest experimentally determined electron affinity,[23] and high electron affinities are also found for the lower fluorides of platinum.[21] Therefore, we investigated the structure and stability of the platinum fluorides PtF_n ($n = 2, 4, 6, 8$) with an emphasis on their electron affinities.

Computational Details

For platinum we used the scalar relativistic energy-consistent small-core pseudopotential of the Stuttgart group to replace the 60 core electrons.[24] In the geometry optimization, the Pt basis set described in ref 25 was reduced to a contracted (9s8p7d)/[7s6p6d] basis set. Two diffuse s functions and an optimized f exponent of 1.2178 augmented this set for the single point calculations. For fluorine we used the correlation consistent augmented double-ζ basis set of Dunning and co-workers.[26] This resulted in a total number of 248 basis functions for the Hartree−Fock (HF) and subsequent coupled cluster single points of PtF_8. The orbital space was kept fully active throughout. Geometry optimizations, using tight convergence criteria to detect possible small Jahn−Teller symmetry breaking effects, and frequency calculations

---

* To whom correspondence should be addressed.

(1) Bartlett, N. Valency in the Periodic Table−Concerning the Limits of Oxidation of the Elements. In *32nd Proceedings of the Robert A. Welch Foundation*; Houston, Texas, 1988; p 259.
(2) Pyykkö, P.; Runeberg, N.; Straka, M.; Dyall, K. G. *Chem. Phys. Lett.* **2000**, *328*, 413.
(3) Bartlett, N.; Yeh, S.; Kourtakis, K.; Mallouk, T. *J. Fluorine Chem.* **1984**, *26*, 97.
(4) Bartlett, N.; Beaton, S. P.; Reeves, L. W.; Wells, E. J. *Can. J. Chem.* **1964**, *42*, 2531.
(5) Glemser, O.; Roesky, H. W.; Hellberg, K. H.; Werther, H. U. *Chem. Ber.* **1966**, *99*, 2652.
(6) Veldkamp, A.; Frenking, G. *Chem. Ber.* **1993**, *126*, 1325.
(7) Bartlett, N.; Sladky, F. O. The Chemistry of Krypton, Xenon and Radon. In *Comprehensive Inorganic Chemistry*; Trotman-Dickenson, A. F., Ed.; Pergamon Press: Oxford, 1973; Vol 1, p 213.
(8) Pyykkö, P. *Chem. Rev.* **1988**, *88*, 563.
(9) Pyykkö, P.; Desclaux, J. P. *Acc. Chem. Res.* **1979**, *12*, 276.
(10) Schwerdtfeger, P.; Boyd, P. D. W.; Brienne, S.; Burrell, A. K. *Inorg. Chem.* **1992**, *31*, 3411.
(11) Seth, M.; Cooke, F.; Pelissier, M.; Heully, J.-L.; Schwerdtfeger, P. *J. Chem. Phys.* **1998**, *109*, 3935.
(12) Kaupp, M.; von Schnering, H. G. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 861.
(13) Kaupp, M.; Dolg, M.; Stoll, H.; von Schnering, H. G. *Inorg. Chem.* **1994**, *33*, 2122.
(14) Weinstock, B.; Claassen, H. H.; Malm, J. G. *J. Am. Chem. Soc.* **1957**, *79*, 5832.
(15) Bare, W. D.; Citra, A.; Chertihin, G. V.; Andrews, L. *J. Phys. Chem. A* **1999**, *103*, 5456.
(16) Steimle, T. C.; Jung, K. Y.; Li, B.-Z. *J. Chem. Phys.* **1995**, *103*, 1767.
(17) Chung, S.-C.; Krüger, S.; Pacchioni, G.; Rösch, N. *J. Chem. Phys.* **1995**, *102*, 3695.
(18) Korobov, M. V.; Bondarenko, A. A.; Sidorov, L. N.; Nikulin V. V. *High Temp. Sci.* **1983**, 411.
(19) Korobov, M. V.; Nikulin, V. V.; Chilingarov, N. S.; Sidorov, L. N. *J. Chem. Thermodyn.* **1986**, *18*, 235.
(20) Kuznetsov, S. V.; Korobov, M. V.; Sidorov, L. N.; Sadinova, L. N.; Shipachev, V. A.; Mitkin, V. N. *Int. J. Mass Spectrom. Ion Processes* **1989**, *87*, 1.
(21) Kuznetsov, S. V.; Korobov, M. V.; Sidorov, L. N.; Shipachev, V. A.; Mitkin, V. N. *Int. J. Mass Spectrom. Ion Processes* **1989**, *87*, 13.
(22) Holloway, J. H.; Stanger, G.; Hope, E. G.; Levason, W.; Ogden, J. S. *J. Chem. Soc., Dalton Trans.* **1988**, 1341.
(23) Gutsev, G. L.; Boldyrev, A. I. *Adv. Chem. Phys.* **1985**, *61*, 169.
(24) Stoll, H.; Dolg, M.; Preuss, H. *Pseudopotential parameters and basis sets*; Internal Report, Universität Stuttgart, Stuttgart, 1997, and references therein.
(25) Wesendrup, R.; Laerdahl, J. K.; Schwerdtfeger, P. *J. Chem. Phys.* **1999**, *110*, 9457.
(26) Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6769.

10.1021/ic010169t CCC: $20.00

were performed at the density functional B3LYP level using Gaussian98 followed by a thermodynamical analysis for the various decomposition processes of PtF_{2n} ($n = 1, 2, 3, 4$).[27] The optimized structures for the neutral species are all minima as checked by frequency analyses.[28] The singlet−triplet energy separation was determined for the structures where the triplet state represents the electronic ground state. Quintet states for the neutral and quartet states for the anionic species are too high in energy and were not considered. A comparison of different minimum structures for PtF_2 optimized at B3LYP, Møller−Plesset second-order (MP2), and CCSD(T) level reveals a reasonable agreement between the methods and justifies our choice of the less expensive B3LYP method for the geometry optimization. For the higher fluorides, coupled cluster single points were calculated at the B3LYP geometries using the program AcesII.[29] To obtain the vertical electron affinities (EA), the energies of the anions were calculated at the geometry of the corresponding neutral molecules. For comparison we also optimized the structures of PtF_2^-, PtF_4^-, and PtF_6^- to determine the adiabatic electron affinities. As the difference between both EAs is minute, only the vertical EA was calculated for PtF_8. The doubly charged free species PtF_2^{2-} and PtF_4^{2-} are not stable with respect to loss of an electron according to our computations and will therefore not be discussed. Although spin−orbit splitting is significant in the platinum atom, its importance generally decreases with increasing number of ligands. Spin−orbit effects were therefore neglected.

Results and Discussion

The optimized B3LYP structures are shown in Figures 1 and 2. In the following we discuss the fluorides according to their coordination number.

PtF_2. For the electronic ground state of the platinum atom, triplet and singlet electronic states are almost degenerate.[30] Therefore, both multiplicities need to be considered here. Table 1 summarizes the two lowest singlet and triplet states for PtF_2 as optimized at the B3LYP, the MP2, and the CCSD(T) levels of theory. The MP2 structures, displaying the familiar tendency for overbinding of this method, are characterized by slightly shorter bonds as compared to the B3LYP or CCSD(T) structures. Apart from that, the overall agreement between the geometric parameters is quite satisfactory. Most importantly, all three methods qualitatively reproduce the energetic order of the different structures.

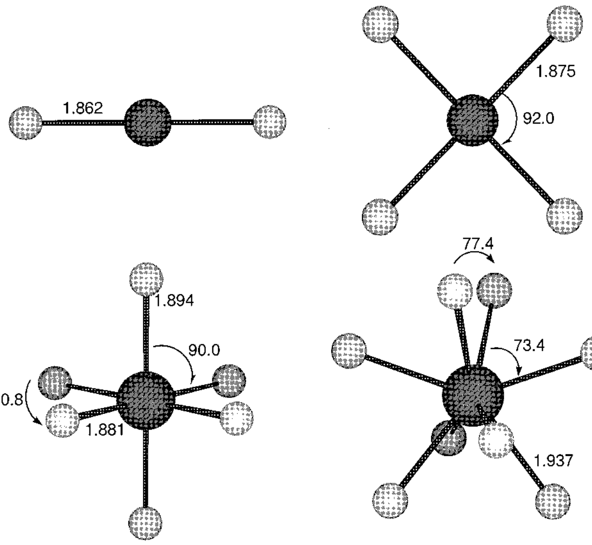

Figure 1. B3LYP optimized structures for the neutral platinum fluorides. Distances in Å and angles in degrees.

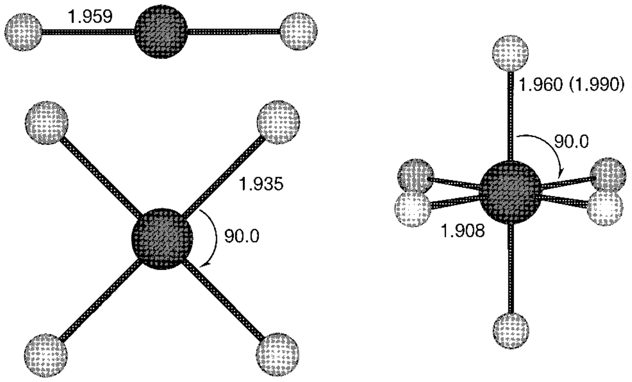

Figure 2. B3LYP optimized structures for the singly charged anionic platinum fluorides. Distances in Å and angles in degrees. PtF_6^{2-} is an ideal octahedron, and the Pt−F bond distance is given in parentheses.

Table 1: Comparison of Structures, Energies, and Vibrational Frequencies for Some Low-lying States of PtF_2 Using Different Methods[a]

state	property	B3LYP	MP2	CCSD(T)
$D_{\infty h}$ ($^3\Sigma_g^+$)	r_e	1.862	1.848	1.857
	$\omega_e(\Pi_u)$	138	136	141
	$\omega_e(\Sigma_u^+)$	638	679	657
	$\omega_e(\Sigma_g^+)$	703	729	708
$D_{\infty h}$ ($^3\Pi_u$)	r_e	1.904	1.895	1.900
	$\omega_e(\Pi_u)$	151	156	163
	$\omega_e(\Sigma_u^+)$	651	655	664
	$\omega_e(\Sigma_g^+)$	622	638	639
	ΔE	30.1	40.2	47.3
C_{2v} ($^1A_1$)	r_e	1.870	1.846	1.856
	θ	125.6	127.9	133.1
	$\omega_e(A_1)$	149	124	116
	$\omega_e(A_1)$	638	675	659
	$\omega_e(B_1)$	632	755	667
	ΔE	98.6	93.1	112.0
$D_{\infty h}$ ($^1\Sigma_g^+$)	r_e	1.951	1.943	1.946
	$\omega_e(\Pi_u)$	159	180	171
	$\omega_e(\Sigma_u^+)$	600	598	602
	$\omega_e(\Sigma_g^+)$	600	627	618
	ΔE	135.4	123.1	122.8

[a] Equilibrium bond distances r_e in Å, bond angles θ in degrees, harmonic frequency ω_e in cm^{-1}, and energy difference ΔE in kJ/mol as compared to the linear $^3\Sigma_g^+$ ground electronic state.

The ground state of PtF_2 appears to be a linear $^3\Sigma_g^+$ state with a Pt−F bond length of 1.857 Å at the CCSD(T) level. This is in contrast to PtH_2, which has a $^1A_1$ (C_{2v}) electronic ground state.[31] The first excited state ($^3\Pi_u$) is also linear and

---

(27) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratman, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.1; Gaussian, Inc.: Pittsburgh, PA, 1998.

(28) For future gas-phase spectroscopic studies we list the B3LYP normal frequencies for the platinum fluorides in their electronic ground state (in cm^{-1}). **PtF_2 ($D_{\infty h}$):** 138 (Π_u), 638 (Σ_u^+), 703 (Σ_g^+). **PtF_4 (D_{2h}):** 161 (Au), 224 (B_{2u}), 232 (B_{3u}), 249 (B_{1u}), 270 (A_g), 318 (B_{3g}), 664 (A_g), 684 (B_{2u}), 692 (B_{1u}). **PtF_6 (D_{2h}):** 163 (B_{2u}), 212 (B_{1u}), 218 (A_g), 225 (A_g), 233 (B_{3g}), 255 (A_u), 265 (A_g) 276 (B_{1u}), 285 (B_{3u}), 615 (A_g), 646 (A_g), 659 (B_{3g}), 667 (B_{3u}), 680 (B_{2u}), 680 (B_{1u}). **PtF_8 (D_4):** 125 (B_1), 126 (B_2), 205 (A_1), 283 (E), 301 (A_2), 316 (E), 345 (E), 346 (A_1), 396 (B_2), 397 (B_1), 485 (B_2), 487 (B_1), 509 (E), 583 (A_2), 585 (A_1), 595 (E).

(29) Stanton, J. F.; Gauss, J.; Watts, J. D.; Nooijen, M.; Oliphant, N.; Perera, S. A.; Szalay, P. G.; Lauderdale, W. L.; Gwaltney, S. R.; Beck, S.; Balková, A.; Bernholdt, D. E.; Baeck, K.-K.; Sekino, H.; Bartlett, R. J. *ACES II*; University of Florida: Gainesville, 1995.

(30) Moore, C. E. *Atomic Energy Levels*; US GPO: Washington, 1958.

Table 2: Calculated and Experimental Reaction Energies in KJ/mol for the Reaction of $PtF_{2n} + F_2$ ($n = 0-3$)[a]

method	$Pt + F_2 \rightarrow PtF_2$	$PtF_2 + F_2 \rightarrow PtF_4$	$PtF_4 + F_2 \rightarrow PtF_6$	$PtF_6 + F_2 \rightarrow PtF_8$
HF	−562.6	−238.7	85.8	577.4
MP2	−688.8	−352.9	−289.2	90.2
CCSD	−663.5	−308.9	−113.4	304.4
CCSD(T)	−677.7	−337.6	−172.1	229.7
B3LYP	−606.2	−335.4	−183.9	306.4
$\Delta G°$	−692.3	−379.3	−233.4	281.0
$\Delta S°$	74.2	−139.9	−167.4	−183.1
$\Delta H°$	−670.2	−335.4	−160.7	226.5
$\Delta H°$ (exp.)	−674 ± 25	−414 ± 50	−155 ± 53	−

[a] Experimental values from refs 18, 19, and 34. Calculated energy differences in kJ/mol, standard enthalpies, $\Delta H°$, and Gibbs free energies, $\Delta G°$, in kJ/mol, and entropies, ΔS, in J/K for the reaction of $PtF_{2n} + F_2$ ($n = 0-3$) at standard conditions (1atm pressure and 298.15 K). For the thermodynamic data, CCSD(T) energies and thermal corrections from B3LYP frequency calculations were used.

possesses with 1.90 Å slightly elongated Pt−F bonds. Experimentally the structure of platinum difluoride is not known, but our calculated bond length lies in the range of the linear PtF_2 fragment as it occurs in hexacoordinated platinum complexes. Here the Pt−F distances range from 1.83 Å for PtF_6 to 1.94 Å for *trans*-$[PtX_2(Py)_4]^{2+}$.[32,33]

In their thermodynamical analysis of PtF_2, Korobov and coworkers assumed a bent structure.[18] According to our calculations the lowest C_{2v} minimum lies about 100 kJ/mol above the linear global minimum and corresponds to a singlet state. We note, however, that at the experimental temperature of 850−1120 K a number of excited electronic states, corresponding to both geometries, will be populated.[18]

If we use a value of 565 kJ/mol as the atomization energy for platinum, we obtain −674 ± 25 kJ/mol as the experimental enthalpy for the reaction of $Pt + F_2 \rightarrow PtF_2$.[34] This agrees excellently with our calculated standard reaction enthalpy of $\Delta H° = -670$ kJ/mol derived from CCSD(T) electronic energies and B3LYP harmonic frequencies (see Table 2).

The HF results deviate from the correlated energies not only for PtF_2 but also for all molecules under investigation. Not surprisingly, correlation is essential to obtain any meaningful results, and we list the HF values for reasons of completeness only, without further discussion. However for PtF_2, also the B3LYP value of 606 kJ/mol is significantly too low, even when the large error of the experimental reaction enthalpy and the fact that we neglect anharmonicity effects in our thermochemical analysis are taken into account.

For the vertical electron affinity we obtain values between 2.72 and 3.13 eV, Table 3. The optimized ground state for PtF_2^- corresponds to a linear $^2\Pi_g$ state with significantly elongated Pt−F bonds of 1.959 Å. Despite this structural difference, the adiabatic electron affinity is only moderately greater than the corresponding vertical values, with deviations between 0.07 eV (MP2) and 0.17 eV (B3LYP). Naturally, the difference is most pronounced at the B3LYP level, which was used to optimize both the neutral and anionic structures. To the best of our knowledge, the experimental electron affinity of PtF_2 has never been published. In light of our results for the higher fluorides, a value of 3.0 ± 0.3 eV appears to be reasonable.

PtF_4. In contrast to the assumption by Korobov and coworkers, the tetrahedral structure is not a minimum on the PtF_4 hypersurface, but a second-order saddle point.[18] Instead the low-lying singlet and the triplet states of PtF_4 correspond to D_{4h} structures, or to be more precise a slightly Jahn−Teller distorted D_{2h} structure. Given the plethora of planar tetracoordinated platinum complexes known, our finding is hardly a surprise. Neither for the singlet or the triplet state any low energy minima of lower symmetry could be found, so we restrain our discussion to the D_{4h} structure.

Table 3: Calculated and Experimental Electron Affinities in eV for the Platinum Fluorides[a]

molecule	HF	MP2	CCSD	CCSD[T]	B3LYP	exp
Pt	0.55	1.65	1.69	1.85	2.02	2.12
F	1.39	3.54	3.13	3.23	3.60	3.40
PtF_2	2.09	3.01	2.73	2.72	3.13	
PtF_2 (ad.)	2.33	3.08	2.87	2.86	3.30	−
PtF_4	5.38	5.48	5.47	5.24	5.12	
PtF_4 (ad.)	5.25	5.51	5.48	5.29	5.35	5.50 ± 0.25[b]
PtF_6	8.66	6.50	7.57	7.01	6.68	
PtF_6 (ad.)	8.30	6.43	7.43	6.95	6.78	7.00 ± 0.35[c]
PtF_6^-	1.37	0.19	0.76	0.37	0.36	3.9 ± 0.6[c]
PtF_8	7.32	5.96	6.65	6.23	6.62	−

[a] Adiabatic electron affinities using optimized structures of the corresponding anions are denoted by (ad.). [b] Reference 20. [c] Reference 21.

The orbital situation of the singlet ground state is characterized by fully occupied HOMOs of e_g symmetry and a b_{2g} LUMO, thus giving rise to a $^1A_1$ electronic ground state. For the triplet state the orbital order is slightly different, as the b_{2g} orbital lies below the degenerated e_g orbitals and above the a_{1g} orbital. Independent of the exact orbital energies, the distribution of six electrons into these four orbitals can lead to four close lying triplet states. Occupation of b_{2g} and a_{1g} and leaving both e_g orbitals singly occupied gives rise to a $^3A_{2g}$ state. Note that the other possible products of $e_g \times e_g$ result in a symmetric spatial wave function that cannot validly be combined with a triplet spin function. If both e_g orbitals are fully occupied, a $^3B_{2g}$ state results from the combination $a_{1g} \times b_{2g}$. Finally, E_g states are obtained from either the occupation $e_g \times a_{1g}$ or from $e_g \times b_{2g}$. Symmetry arguments suggest that the E_g state cannot correspond to a true minimum in D_{4h} but undergoes Jahn−Teller distortion along a B_1 or B_2 mode.[35] Indeed, a careful optimization reveals a slightly distorted structure of D_{2h} symmetry as the global minimum for PtF_4 at the B3LYP level, with alternating bond angles of 92.08 and 87.92°. Again, the situation is quite different to that of PtH_4, where a $^1A''$ ground state of C_s symmetry has been determined.[31]

As summarized in Table 4, the stationary points for PtF_4 are quite similar with respect to bond distances and relative energies. Clearly, further studies, including spin−orbit coupling within a multireference procedure, would be necessary to determine accurately the ground-state structure of PtF_4. However, it appears

---

(31) Andrews, L.; Wang, X.; Manceron, L. *J. Chem. Phys.* **2001**, *114*, 1559.
(32) Brisdom, A. K.; Holloway, J. H.; Hope, E. G.; Levason, W.; Ogden, J. S.; Saad, A. K. *J. Chem. Soc., Dalton Trans.* **1992**, 139.
(33) Drews, H.-H.; Preetz, W. *Z. Anorg. Allg. Chem.* **1997**, *623*, 509.
(34) Lias, S. G.; Liebman, J. F.; Levin, R. D.; Kafafi, S. A. *NIST Standard Reference Database, Positive Ion Energetics*, Version 2.01; January, 1994.
(35) Jotham, R. W.; Kettle, S. F. A. *Inorg. Chim. Acta* **1971**, *5*, 183.

Table 4: Single Point Energies for Some Low-lying States of PtF_4 Using Different Methods[a]

state		B3LYP	MP2	CCSD(T)
D_{2h} ($^3B_{2g}$)	r_e	1.875		
D_{4h} (^3E_g)[b]	r_e	1.879		
	ΔE	6.3	−2.8	−2.3
D_{4h} ($^3A_{2g}$)	r_e	1.887		
	ΔE	10.8	0.8	10.6
D_{4h} ($^3B_{2g}$)	r_e	1.903		
	ΔE	70.4	37.9	55.9
D_{4h} ($^1A_{1g}$)	r_e	1.870		
	ΔE	77.3	18.2	61.5

[a] Bond distances r_e in Å, differences in energy ΔE in kJ/mol as compared to the D_{2h} ground state. [b] Second-order saddle point.

certain that the ground state of PtF_4 is a triplet state. Fortunately, the near degeneracy of the different states implies that the actual nature of the ground state is less important for the calculation of reaction enthalpies and electron affinities. All our calculated energy differences for the reaction $PtF_2 + F_2 \rightarrow PtF_4$ are below the experimental value of 414 kJ/mol (Table 2). This may well indicate that the correct experimental value lies at the lower end of the substantial error margin of 50 kJ/mol.

Both vertical and adiabatic EAs agree excellently with the reported experimental values of 5.50 eV. The optimized structure for PtF_4^- is a $^2B_{2g}$ state of square-planar symmetry with Pt−F bonds of 1.935 Å. As expected, the structural changes upon addition of an electron are less pronounced in PtF_4 as compared to PtF_2.

PtF_6. Unlike the di and tetrafluoride, platinum hexafluoride is a volatile molecule even at room temperature and has been reported as early as 1957.[14] Since then it has been the subject of numerous experimental and some theoretical studies.[19,21,32,36−40] It is generally described as octahedral monomer, but small distortions from octahedral symmetry were found in the solid state.[38] The ground-state configuration of octahedral PtF_6 is (5d t_{2g})^4, corresponding to a triplet ground state. Of the possible combinations resulting from $t_{2g} \times t_{2g}$, only the $^3T_{1g}$ state is symmetry allowed and has been postulated as the ground state for PtF_6 based on its magnetic moment.[41] However, octahedral molecules of $^3T_{1g}$ symmetry are subject to a first-order Jahn−Teller effect and distort along an E_g or T_{2g} vibrational mode.[35] This prediction is reproduced by our calculations. The optimized octahedral PtF_6 has a bond length of 1.887 Å; this is somewhat longer than the experimental value, which varies between 1.839 and 1.853 Å, depending on the respective experimental method.[36−40] More importantly however, the calculated octahedral structure is a second-order saddle point, and the frequency analysis reveals a doubly degenerated imaginary frequency of 70i cm^{-1} and thus an E_g distortion. Optimization along these coordinates leads to a true minimum of D_{2h} symmetry that lies only 4 kJ/mol below the octahedral geometry. Clearly, this energy difference is too small to be experimentally detectable. Under most experimental conditions−with the exception of matrix experiments−PtF_6 will be fluctuating between degenerated D_{2h} minima via transition states close to the octahedral symmetry, thus yielding an averaged experimental result.

The lowest singlet state of PtF_6 corresponds to C_{2h} symmetry and can be regarded as a slightly distorted octahedron, too. The triplet−singlet gap amounts to 72 kJ/mol. Several minima of lower symmetry could also be located for both spin states, but they lie significantly higher in energy.

Our calculated values for the reaction $PtF_4 + F_2 \rightarrow PtF_6$ are spread over a wide range, but the B3LYP and CCSD(T) values match the experimental result quite nicely. We note that MP2 performs less well for higher oxidation states and for PtF_6 deviates drastically from CCSD(T) results as this was found previously for the Group 11 fluorides.[11] We conclude that CCSD(T) calculations are indeed necessary to obtain reliable energies for the platinum fluorides.

Our calculated electron affinities lie around 7 eV, which is in excellent agreement with the most recent experimental value by Korobov et al.[21] Clearly, earlier values of 8.0 and 9.06 eV can be discarded.[36,42] Not surprisingly, the difference between the calculated vertical and adiabatic EAs is even smaller for PtF_6 than for PtF_4. The optimized structure for octahedral PtF_6^- has a bond length of 1.927 Å. Like the neutral hexafluoride, PtF_6^- is subject to a Jahn−Teller effect. It distorts to D_{4h} geometry with elongated axial bonds of 1.960 Å and equatorial bonds of 1.908 Å. Interestingly, the dianion PtF_6^{2-} is also thermodynamically stable. With a configuration of (5d t_{2g}^6), it has a $^1A_{1g}$ ground state of perfect octahedral symmetry and Pt−F bonds of 1.990 Å. For comparison, in the solid state, two additional electrons increase the Pt−F bond length from 1.85 Å for PtF_6 to 1.92 Å for PtF_6^{2-}.[43] In the crystal the differences between the neutral and the dianion are moderated by the influence of the lattice and, therefore, are less pronounced than for isolated gas-phase molecules, as calculated here. The calculated *second* EA of PtF_6 is 0.37 eV at CCSD(T) and 0.36 eV at B3LYP, slightly higher than a recent density functional result of 0.l eV,[39] with our MP2 and CCSD values scattered around that number. It is therefore safe to conclude that the reported experimental value of 3.9 eV is much too high, possibly due to excited states of the singly charged PtF_6^- involved in the experiment.[21]

PtF_8. Unlike the lower fluorides, PtF_8 has a singlet ground state. The global minimum appears to be of D_4 symmetry, a slightly distorted square antiprism. Although no imaginary frequencies appear in the frequency analysis and PtF_8 represents a true minimum, the compound is only metastable. Decomposition to PtF_6 and molecular fluorine is exothermic by 306 kJ/mol at the B3LYP level and by 90 kJ/mol even at the MP2 level. The low stability of PtF_8 is reflected by the Pt−F bond length of 1.937 Å, which is significantly longer as compared to the lower oxidation state platinum fluorides. Not surprisingly, the EA of PtF_8 lies with values between 5.96 eV (MP2) and 7.73 eV (HF) below the corresponding values of the hexafluoride. Accordingly, the anion will be even *less* stable toward loss of F_2 than neutral PtF_8. It is therefore most unlikely that PtF_8 will ever be observed experimentally.

Acknowledgment. This work was supported by Deutsche Forschungsgemeinschaft (Bonn, Germany), the Marsden Fund (Wellington), and the Auckland University Research Committee.

IC010169T

---

(36) (a) Bloor, J. E.; Sherrod, R. E. *J. Am. Chem. Soc.* **1980**, *102*, 4333. (b) Gutsev, G. L.; Boldyrev, A. I. *Chem. Phys. Lett.* **1983**, *101*, 441.
(37) McDowell, R. S. *Spectrochim. Acta*, **1986**, *42A*, 1053.
(38) Marx, R.; Seppelt, K.; Ibberson, R. M. *J. Chem. Phys.* **1996**, *104*, 7656.
(39) Macgregor, S. A.; Moock, K. H. *Inorg. Chem.* **1998**, *37*, 3284.
(40) Richardson, A. D.; Hedberg, K.; Lucier, G. M. *Inorg. Chem.* **2000**, *39*, 2787.
(41) Moffit, W.; Goodman, G. L.; Weinstock, B. *Mol. Phys.* **1959**, *2*, 109.
(42) Nikitin, M. I.; Sidorov, L. N.; Korobov, M. V. *Int. J. Mass Spectrom. Ion Processes* **1981**, *39*, 13.
(43) Graudejus, O.; Wilkinson, A. P.; Chacón, L. C.; Bartlett, N. *Inorg. Chem.* **2000**, *39*, 2794.