Validation of the Existence of Tetrameric Species of Potassium Trimethylsilanolate in the Gas Phase with a Theoretical Cluster Model: Role of the Counterion as Charge Localizer in the Structure

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We have investigated, theoretically, the structural properties of potassium trimethylsilanolate in the gas phase at a B3LYP/6-31+G* level. For this purpose, a simplified ionic cluster model based on potassium trimethylsilanolate tetramers, proposed in the literature as the structural units of this compound in the solid state, was developed. Furthermore, we compared the validity of the model with two simpler ones: a monomer of potassium trimethylsilanolate and a trimethylsilanolate anion in the gas phase. The developed ionic cluster model was found to be best in reproducing the experimental structure of potassium trimethylsilanolate, supporting, at the same time, the existence of such tetrameric species (previously identified experimentally from mass spectrometry data by Weiss et al.) in the gas phase. Finally, NBO calculations highlighted the important role of the potassium counterion as a charge localizer in the structure of these chemical species.

Introduction

A considerable number of recent studies deal with the synthesis and structural characterization of different metallic alkylsilanolates. These compounds have increasingly attracted the attention of several disciplines, such as material science and catalysis, due to their potential applications in the preparation of inorganic materials with improved physical properties.[1,2] Although extensively studied experimentally (mainly by NMR and X-ray diffraction techniques), theoretical investigations on these structures are rare. In recent years, however, there has been a growing interest in combined theoretical and experimental studies that deal with the bonding properties and molecular structures of compounds containing highly polar bonds of the type M−X (where M = metal and X = C, O, ...).[3] The system studied in the present work, potassium trimethylsilanolate, belongs to this family of compounds.

The crystal and molecular structures of potassium trimethylsilanolate have been studied previously by X-ray diffraction (XRD) and mass spectrometry. Weiss et al.[4] were first to solve the crystal structure of this compound, from powder XRD data, in the cubic space group $P\bar{4}3m$ ($R = 7.9\%$). In the Weiss structure, potassium trimethylsilanolate forms tetrameric units (Figure 1) where the oxygen and potassium atoms are arranged in a slightly distorted cube. The authors also suggested the existence of these tetrameric units in the gas phase from mass spectrometry experiments. Years later, Pauer and Sheldrick[5] redetermined the crystal structure from single-crystal XRD data. A tetramer unit was also proposed as the main building block. However, the four trimethylsilanolate groups were found to be in a staggered conformation (caused by a 19.5° rotation of the methyl groups) in contrast to an eclipsed one proposed in ref
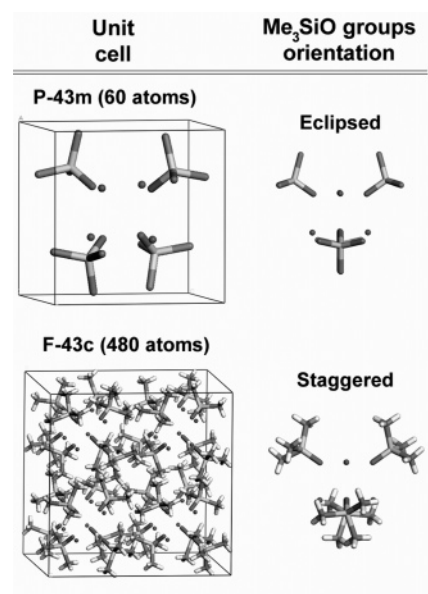
Figure 1. Unit cell and tetrameric unit representations of the experimental crystal structures of potassium trimethylsilanolate determined by Weiss (upper) and Pauer (lower).

4. Pauer's unit cell contains eight tetrameric units distributed in the eight vertexes of a distorted cube, leading to an F-centered lattice that belongs to the space group $F\bar{4}3c$ ($R = 2.27\%$). Both tetrameric structural units and unit cell representations are shown in Figure 1.

We notice considerable structural differences between both experimental structures: the main ones are the space group symmetry and the relative orientation of the trimethylsilanolate groups (eclipsed in ref 4 and staggered in ref 5). From an experimental viewpoint, the structure proposed by Pauer and Sheldrick is more accurate as it was solved from single crystal
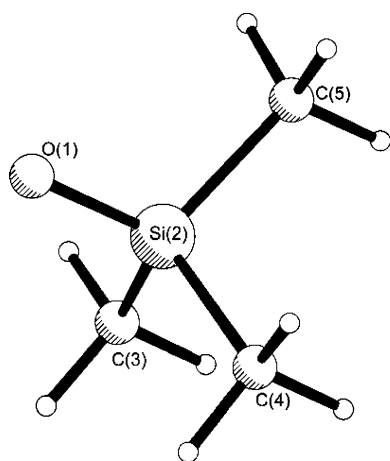
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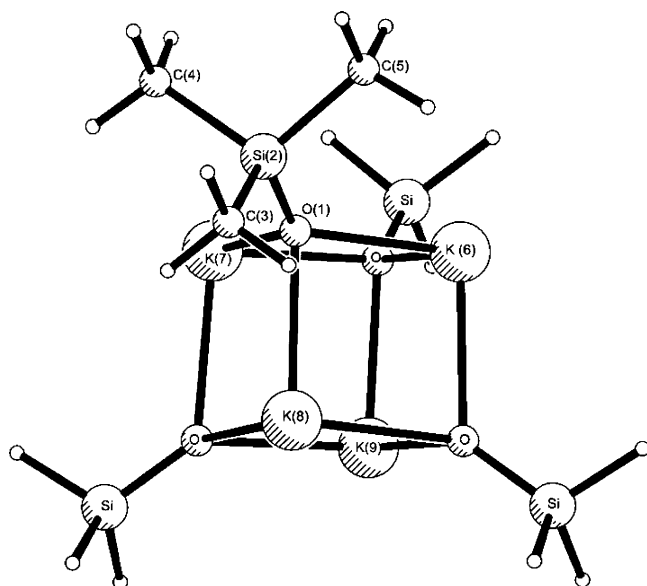
Figure 2. Molecular representation and atom numbering for the ionic cluster model.
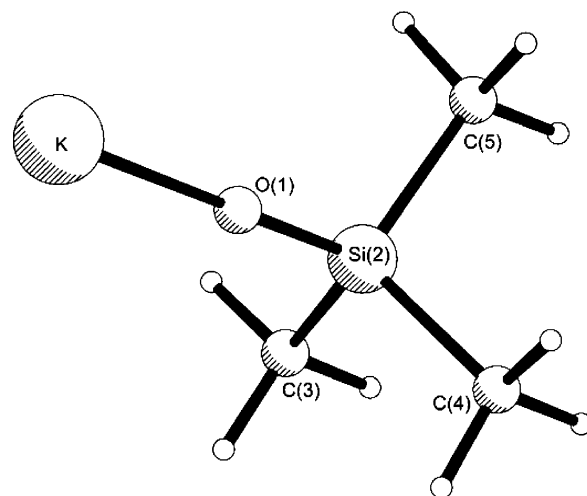

Figure 3. Molecular representation and atom numbering for the trimethysilanolate anion.

diffraction data, instead of powder, with a much lower goodness-of-fit function ($R = 2.29\%$ compared to 7.9% of the Weiss structure).

One of the principal aims of the present work has been to validate and support, using theoretical models, the existence of the isolated tetrameric units of potassium trimethylsilanolate in the gas phase that Weiss et al.[4] proposed from mass spectrometry data. Because of the considerable size of the tetrameric unit cluster, the model was simplified by partially substituting three of the SiMe$_3$ groups by SiH$_3$. The simplified model was then optimized in the gas phase at a DFT/B3LYP/6-31+G* level of theory.

Geometry optimizations of the isolated trimethysilanolate anion and a monomer of potassium trimethylsilanolate, at the same level of theory, were carried out in order to compare the different model performances in reproducing the geometric parameters reported in the literature.[4,5] Additionally, some spectroscopic evidence,[6] which supports our ionic cluster model, was also brought forward.

Finally, NBO calculations were also implemented in order to analyze the electronic structure of the system. The potassium cations were found to play an important role in the stability of the system since they function as charge localizers in the structure.

Figure 4. Molecular representation and atom numbering for the trimethylsilanolate monomer.

Computational Details

All theoretical calculations in this work were performed with the Gaussian 03 program package.[7] The models K$_4$((OSiMe$_3$)-(OSiH$_3$)$_3$), KOSiMe$_3$, and (OSiMe$_3$)$^-$ were optimized at the DFT/B3LYP/6-31+G* level.

Natural bond orbital calculations[8] on the optimized structures of all three models were performed with the NBO 3.1 program[9] as implemented in Gaussian 03.

Results and Discussion

Theoretical Models. The ionic cluster model defined is based on the tetramers of potassium trimethylsilanolate that both refs 4 and 5 indicated as the structural units (from X-ray diffraction experimental data) of the species in the solid phase. Remarkably, as mentioned above, Weiss et al. even detected the presence of these tetramers in the gas phase by mass spectrometry.[4] Our ionic cluster model was simplified, because of the considerable size of the initial tetramers proposed in the literature, by substituting three of the four −SiMe$_3$ groups by −SiH$_3$ groups. The resulting model has 33 instead of 60 atoms and the following formula: K$_4$((OSiMe$_3$)(OSiH$_3$)$_3$). This strategy could be also applied in the case of other metallic silanolates that are known to be arranged following patterns similar to that of potassium trimethylsilanolate.[1,2]

As the starting point of the optimization, the trimethysilanolate group and the three −SiH$_3$ groups were rotated with respect to the diagonal of the distorted cube, determined by the oxygen and potassium atoms, by approximately 20° as in ref 5. However, the observed staggered conformation of the trimethyl group was not found to be a minimum of the potential energy surface (PES) in the gas phase. Instead, a C_1 structure in which the trimethylsilanolate group adopts an anti conformation with respect to the diagonal of the cube (Figure 2) was obtained (a real minimum in the PES since it resulted in no negative frequencies calculated). Similarly, the −SiH$_3$ groups also adopted an anti conformation with respect to the diagonal of the cube.

A simpler cluster model in which all the trimethylsilanolate groups were substituted by SiH$_3$ groups, K$_4$(OSiH$_3$)$_4$, was also optimized at a B3LYP/6-31+G* level of theory in order to assess the preferred conformation of the −SiH$_3$ groups within a cluster of higher symmetry. Four imaginary frequencies, corresponding to the −SiH$_3$ deformation vibrations, were calculated for the eclipsed conformation of the four −SiH$_3$

TABLE 1: Experimental and B3LYP/6-31+G* Optimized Geometric Parameters of Three Models (Bond Distances in Angstroms, Angles in Degrees) of Potassium Trimethylsilanolate

	experiment		B3LYP/6-31+G*		
parameter	ref 4[a]	ref 5[b]	ionic cluster[c]	KOSiMe$_3$	[OSiMe$_3$]$^-$
r(Si$_2$O$_1$)	1.60	1.580	1.628	1.617	1.587
r(Si$_2$C$_3$)	1.81	1.879	1.907	1.912	1.936
r(Si$_2$C$_4$)			1.909	1.912	
r(Si$_2$C$_5$)			1.910	1.912	
r(Si$_2$O$_1$−OSi)	3.602	3.697	3.884	-	-
r(O$_1$K$_6$)	2.601	2.629	2.649	2.326	-
r(O$_1$K$_7$)			2.653		
r(O$_1$K$_8$)			2.647		
∠(O$_1$Si$_2$C$_3$)	110	112.5	111.6	112.3	114.9
∠(O$_1$Si$_2$C$_4$)			111.7	112.3	
∠(O$_1$Si$_2$C$_5$)			112.1	112.3	
∠(C$_4$Si$_2$C$_3$)	109	106.3	107.1	106.5	103.5
∠(C$_4$Si$_2$C$_5$)			107.1	106.5	
∠(C$_3$Si$_2$C$_5$)			106.9	106.6	

[a] Crystalline powder X-ray diffraction. T = 293 K. [b] Single-crystal X-ray diffraction. T = 153 K. [c] Stoichiometry K$_4$((OSiMe$_3$)(OSiH$_3$)$_3$).

TABLE 2: Experimental and Calculated Frequencies (in cm^{-1}), for the Three Theoretical Models, of the SiC and SiO Stretching Normal Modes in Potassium Trimethylsilanolate

B3LYP/6-31+G* (unscaled)				
ionic cluster[a]	KOSiMe$_3$	[OSiMe$_3$]$^-$	solid Raman[b]	assignment
325 (A), 326 (A)	312 (A)		335 m	ν(OK)
584 (A)	587 (A)	558 (A$_1$)	611 vs	ν_s(SiC)
653 (A)	647 (A)	606 (E)	657 m	ν_{as}(SiC)
656 (A)	648 (A)			
985 (A)	1022 (A)	1067 (A$_1$)	986 w	ν(SiO)

[a] Stoichiometry K$_4$((OSiMe$_3$)(OSiH$_3$)$_3$). [b] From ref 6.

groups. All the −SiH$_3$ groups in anti conformation, however, resulted in a real minimum of the PES since no negative frequencies were obtained then.

Additionally, the structures of the isolated trimethylsilanolate anion and the potassium trimethylsilanolate monomer were also optimized taking, in both cases, the experimental structure as starting point. The calculations suggested the trimethylsilanolate anion (Figure 3) to be a symmetric top rotator in C_{3v}, whereas the monomer (Figure 4), optimized with no symmetry restrictions, presented C_1 symmetry.

Theoretical Structure. In Table 1, B3LYP/6-31+G* calculated bond distances and angles for the cluster model, together with those of the isolated anion and monomer, are presented and compared with those determined experimentally.[4,5] As a general trend, the optimized structural parameters for the anion poorly reproduce those of the experimental structure. The SiC bonds and the OSiC angles were clearly overestimated, while the CSiC angle was underestimated.

The experimental geometry is reproduced more accurately with the cluster model. As shown in Table 1, calculated bond distances and angles for the trimethylsilanolate group are in reasonably good agreement with experiment, with the exception of the SiO and SiC bond lengths that were slightly overestimated. In any case, the calculated vibrational frequencies for the stretching normal modes of the SiO and SiC bonds were in better agreement with the experimental bands[6] when the cluster model was used (Table 2).

On the other hand, the SiO−OSi distance, which represents the diagonal of the distorted cube determined by the oxygen and potassium atoms, is also overestimated in the cluster model (Table 1). In this case, the differences found are reasonable as the calculations were done in the gas phase and experiments in the solid state. We attribute the difference in the SiO−OSi distance to the additional long-range electrostatic and short-range packing effects found in the crystalline phase. Similarly,

the final orientation of the trimethylsilanolate group in our simplified ionic cluster model optimized in the gas phase disagrees with that in ref 5 found in the crystal structure. In this case, although the anti conformation is preferred electronically (as shown in the gas-phase calculations), a small change in conformation of the −Si(CH$_3$)$_3$ group at a low conformational energy cost allows a much better crystal packing, and therefore lattice energy.

In summary, our calculations reflect that both the cluster and the monomer models reproduce the experimental structure of the trimethylsilanolate group in a much better way than the isolated anion. Spectroscopic evidence also points to the calculated geometry of the cluster model as the most accurate. Furthermore, the calculations are in better agreement with the experimental structure proposed in ref 5 than the one proposed by Weiss et al.,[4] with the exception of the calculated SiO bond length, which is consistent with the experimental value given in ref 4. Finally, implicit consideration of the potassium counterion clearly improves the performances of the theoretical models. Therefore, to further analyze in which way the presence of the counterion affects the theoretical geometry of potassium trimethylsilanolate, the electronic structures of all the models were studied using the NBO calculations.

Electronic Structure. In NBO terms, the electronic wave function is interpreted as a set of Lewis-type orbitals (formally filled) paired with a set of non-Lewis-type orbitals (formally empty). The electronic interactions within these orbitals and the deviations from the Lewis electronic structure (delocalization effects) are interpreted as charge transfers between the occupied Lewis orbitals (donors) and the theoretically unoccupied non-Lewis orbitals (acceptors). The magnitude of these effects is measured from the analysis of the off-diagonal terms of the Fock matrix. All possible donor−acceptor interactions are taken into account, the strength of which is calculated by second-order perturbation theory.[8]

TABLE 3: Calculated NBO Electronic Populations of the σ and σ^* Orbitals of the SiC and SiO Bonds and the Lone Electron Pairs in the Oxygen Atoms for the Three Models[a]

	NBO populations (au)		
	ionic cluster[a]	KOSiMe$_3$	[OSiMe$_3$]$^-$
σ(Si$_2$C$_3$)	1.974	1.975	1.973
σ(Si$_2$C$_4$)	1.974	1.975	1.973
σ(Si$_2$C$_5$)	1.974	1.975	1.973
σ^*(Si$_2$C$_3$)	0.071	0.072	0.099
σ^*(Si$_2$C$_4$)	0.071	0.072	0.099
σ^*(Si$_2$C$_5$)	0.071	0.072	0.099
σ(Si$_2$O$_1$)	1.988	1.989	1.989
σ^*(Si$_2$O$_1$)	0.038	0.033	0.024
LP(1)(O$_1$)	1.976	1.982	1.981
LP(2)(O$_1$)	1.914	1.910	1.858
LP(3)(O$_1$)	1.913	1.910	1.858
LP*(K$_6$)	0.025	0.008	
LP*(K$_7$)	0.025		
LP*(K$_8$)	0.024		
LP*(K$_9$)	0.022		

[a] The populations of the potassium atom LP* orbitals in the monomer and the ionic cluster models are also given. [b] Stoichiometry K$_4$((OSiMe$_3$)(OSiH$_3$)$_3$).

TABLE 4: Second-Order Perturbation Energy (kcal mol^{-1}) of Some of the More Meaningful Stabilizing Interactions in the Three Models

	$E^{(2)}$ (kcal mol^{-1})		
	ionic cluster[a]	KOSiMe$_3$	[OSiMe$_3$]$^-$
LP(1)(O$_1$) $\rightarrow \sigma^*$(SiC$_3$)			0.71
LP(1)(O$_1$) $\rightarrow \sigma^*$(SiC$_4$)			0.71
LP(1)(O$_1$) $\rightarrow \sigma^*$(SiC$_5$)			0.71
LP(2)(O$_1$) $\rightarrow \sigma^*$(SiC$_3$)		12.31	
LP(2)(O$_1$) $\rightarrow \sigma^*$(SiC$_4$)	10.62	3.08	12.54
LP(2)(O$_1$) $\rightarrow \sigma^*$(SiC$_5$)	7.01	3.08	12.54
LP(3)(O$_1$) $\rightarrow \sigma^*$(SiC$_3$)	11.66		16.72
LP(3)(O$_1$) $\rightarrow \sigma^*$(SiC$_4$)	1.39	9.23	4.18
LP(3)(O$_1$) $\rightarrow \sigma^*$(SiC$_5$)	5.02	9.23	4.18
LP(1)(O$_1$) $\rightarrow$ LP*(K$_6$)	1.97	1.79	
LP(1)(O$_1$) $\rightarrow$ LP*(K$_7$)	1.87		
LP(1)(O$_1$) $\rightarrow$ LP*(K$_8$)	1.95		
LP(1)(O$_1$) $\rightarrow$ LP*(K$_9$)	0.18		
σ(SiO) $\rightarrow$ LP*(K$_6$)	1.26	0.15	
σ(SiO) $\rightarrow$ LP*(K$_7$)	1.15		
σ(SiO) $\rightarrow$ LP*(K$_8$)	1.25		
σ(SiO) $\rightarrow$ LP*(K$_9$)	0.05		

[a] Stoichiometry K$_4$((OSiMe$_3$)(OSiH$_3$)$_3$).

The populations of the σ and σ^* orbitals of the SiC and SiO bonds are presented in Table 3 for the three different models. The different occupations of the antibonding orbitals in the models could explain the differences in the SiC and SiO bond distances calculated for the cluster and the monomer with respect to the isolated anion (see Table 1). The higher population calculated for the antibonding orbitals of the SiC bonds in the trimethylsilanolate anion is related to the existence of stabilizing interactions between these and the lone pairs of electrons on the oxygen atom. Those quantified interactions are given in Table 4. The situation in the orbital populations changes if the counterion is present in the model, since the LP* orbitals of potassium atoms allocate certain amounts of charge (Table 3). As shown in Table 4, in the monomer and the cluster models, stabilizing interactions involving the σ(SiO) and the LP(1) orbitals of the oxygen as well as the LP* orbitals of the potassium atoms are possible and of considerable importance. These interactions could be responsible for the decrease on the OSiC bond angle calculated for the monomer and the cluster.

On the other hand, the different NBO charges calculated on the C atoms (i.e., −1.206 au for the anion, −1.211 au for the

monomer, and −1.219 au for the cluster) suggested that electrostatic repulsion was responsible for the different calculated values of the CSiC angles—sensibly smaller in the anion than in the monomer or the cluster (see Table 1).

Similarly, charge transfer to the potassium atoms were also found in the three −OSiH$_3$ groups of the simplified model. Those also lead to a considerable increase in the population of the LP* orbital of the potassium atoms when compared to the monomer (Table 3).

Furthermore, certain stabilizing interactions were also found between the core orbitals of the potassium atoms and the LP* orbitals of the remaining neighbors. The deletion of these interactions from the NBO scheme leads to an increase in the energy of the system of ca. 22 kcal mol^{-1}.

All these facts point to the key role of the potassium atoms as charge localizers in the structure of trimethylsilanolate. Only when the potassium atoms are considered implicitly in the models is the experimental geometry of the trimethylsilanolate anion reproduced appropriately. The charge transfer calculated between oxygen and potassium atoms can be interpreted as a covalent contribution to the O−K bond. This idea might be reinforced by the observation of a band in the Raman spectrum of potassium trimethylsilanolate at 335 cm^{-1}, calculated for the cluster and the monomer and identified as the O−K stretching but absent in the predicted vibrational spectrum of the isolated anion (see Table 2).

In addition, the high values calculated for the deletion energy of the interaction between the potassium atoms indicates some kind of cooperative effect in the cluster that could, in part, contribute to its existence and stability in the gas phase.

Conclusions

1. The existence and stability of the tetrameric unit of potassium trimethylsilanolate in the gas phase has been validated theoretically using a simplified ionic cluster model, a result that could encourage the experimentalists to try the isolation of these ionic clusters of metallic silanolates.

2. Since the B3LYP/6-31+G* optimized structural parameters for the model reproduced the experimental XRD ones reported in Pauer's study,[5] with the exception of the SiO bond length (whose calculated value was in closer agreement to that in ref 4), the validity of the model has been demonstrated.

3. The optimized anti conformation in the gas phase of the trimethylsilanolate and silyl groups in the cluster model is in disagreement with the experimental observations in the solid phase. The optimization at the same level of a simpler cluster, stoichiometry K$_4$(OSiH$_3$)$_4$, confirmed the preferred anti orientation of the −SiH$_3$ groups since four negative frequencies (corresponding to the deformation vibrations of the silyl group) were obtained when the eclipsed conformation was imposed.

4. The comparative analyses of the optimized geometries calculated for the isolated anion, a monomer, and the simplified ionic cluster with the experimental structure of the potassium trimethylsilanolate salt revealed the importance of considering the counterion implicitly in the models.

5. NBO calculations of the electronic structure corroborated point 4 as a certain charge from the lone pairs of the oxygen and the SiO bonding orbitals was localized in the potassium atoms.

Potassium Trimethylsilanolate Tetrameric Species

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References and Notes

(1) (a) Elvidge, B. R.; Arndt, S.; Spaniol, T. P.; Okuda, J. *Dalton Trans.* **2006**, *20*, 890. (b) Roy, A.; Polarz, S.; Rabe, S.; Rellinghaus, B.; Zähres, H.; Kruis, F. E.; Driess, M. *Chem.—Eur. J.* **2004**, *10*, 1565.

(2) (a) Merz, K.; Block, S.; Schoenen, R.; Driess, M. *Dalton Trans.* **2003**, *17*, 3365. (b) Lerner, H. W.; Scholz, S.; Bolte, M. *Organometallics* **2002**, *21*, 3827. (c) Driess, M.; Merz, K.; Rell, S. *Eur. J. Inorg. Chem.* **2000**, 2517. (d) McGeary, M. J.; Folting, K.; Streib, W. E.; Huffman, J. C.; Caulton, K. G. *Polyhedron* **1991**, *10*, 2699. (e) Schütte, S.; Freire-Erdbrügger, C.; Klingebiel, U.; Sheldrick, G. M. *Phosphorus, Sulfur Silicon* **1993**, *78*, 75. (f) Fuentes, G. R.; Coan, P. S.; Streib, W. E.; Caulton, K. G. *Polyhedron* **1991**, *10*, 2371.

(3) (a) Mohajeri, A.; Abasi, M. J. *Theor. Comput. Chem.* **2006**, *5*, 87. (b) Bickelhaupt, F. M.; Solá, M.; Guerra, C. F. *J. Chem. Theory Comput.* **2006**, *2*, 96. (c) Matito, E.; Poater, J.; Bickelhaupt, F. M.; Solá, M. *J. Phys. Chem. B* **2006**, *110*, 7189. (d) Poleshchunk, O. K. H.; Sevchenko, E. L.; Branchadell, V.; Lein, M.; Frenking, G. *Int. J. Quantum Chem.* **2005**, *101*, 869.

(4) Weiss, E.; Hoffmann, K.; Grztmacher, H. F. *Chem. Ber.* **1970**, *103*, 1190.

(5) Pauer, F.; Sheldrick, G. M.; *Acta. Crystallogr., Sect. C* **1993**, *49*, 1283.

(6) Montejo, M.; Partal Ureña, F.; Márquez, F.; López González, J. J. In *XX Reunión Nacional de Espectroscopía & IV Congreso Ibérico de Espectroscopía: Book of Abstracts*; Ciudad Real, Spain; 2006; p 200.

(7) Frisch, M. J.; et al. *Gaussian 03*, revision C.01; Gaussian Inc.: Wallingford, CT, 2004.

(8) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

(9) Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. *NBO* Version 3.1.