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Linear Ni(I) Complex in *cis*-$[Ni(CN)_4Cl_2]^{5-}$ Cluster

A. A. Leitão,*,[†] N. V. Vugman,[†] and C. E. Bielschowsky[‡]

Instituto de Física and Instituto de Química, Universidade Federal do Rio de Janeiro, Caixa Postal 68528,
Rio de Janeiro, RJ, 21945-970 Brazil

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Ab initio embedded cluster UMP2 calculations are performed on paramagnetic $3d^9$ *cis*-$[Ni(CN)_4Cl_2]^{5-}$ cluster in KCl host lattice taking into account short and long-range crystal interactions. The results confirm the $d_{x^2-y^2}$ unpaired electron orbital assignment, with a small participation of p_x and p_y basis functions. Hyperfine interactions are shown to arise mainly from spin polarization of their valence orbitals caused by the unpaired electron. The calculated difference between the two possible Ni−CN distances is 0.25 Å. Chlorine ions, first neighbors to the central metallic atom, as well as the two cyanides pointing to the $d_{x^2-y^2}$ orbital, are found to be not coordinated to the metal. The coordination complex present in the *cis*-$[Ni(CN)_4Cl_2]^{5-}$ cluster is thus assigned to linear $[Ni(CN)_2]^-$ instead of hexacoordinated or planar forms.

Introduction

Complexes with Ni(I) tetracoordinated or pentacoordinated in their structure have been reported in several works in the literature.[1−10] Ni(I) complexes are paramagnetic, and many of them have been detected by electron paramagnetic resonance[5−10] (EPR). In general, these complexes are obtained by reducing Ni(II) complexes.[1−4] There are some cases where Ni(I) complexes are formed on the surface of supporting materials with different coordinations.[5−7] The paramagnetic Ni(I) complexes can be obtained also as an impurity in the bulk of ionic crystals such as NaCl or KCl.[8−10]

Electron or X-ray irradiation of KCl crystals doped with $[Ni(CN)_4]^{2-}$ coordination complex produces oxidized and reduced paramagnetic forms.[8−10] Altough X-ray irradiation mainly produces square planar paramagnetic complexes,[9,10] it was proposed that electron irradiation also forms this complex in the cis conformation[8] as illustrated in Figure 1A. The *cis*-$[Ni(CN)_4Cl_2]^{5-}$ assignment results from a continuous wave EPR analysis based on measurements of the *g*-tensor components and observation of two distinct ^{13}C isotropic hyperfine couplings (A_{iso}), leading to the identification of two different pairs of equivalent cyanides, which is incompatible with the *trans*-$[Ni(CN)_4Cl_2]^{5-}$ assignment.

However, the exact geometry and total energy for the proposed cis complex, as well as the chlorine positions in the nearby lattice, are not provided by EPR experiments. In fact, EPR data on this species could also lead to other assignments besides the hexa-coordinated *cis*-$[Ni(CN)_4Cl_2]^{5-}$, planar *cis*-$[Ni(CN)_2Cl_2]^{3-}$, or the linear $[Ni(CN)_2]^-$ complex, showed respectively in Figure 1 parts A, B, and C.

In this work, we calculate the *cis*-$[Ni(CN)_4Cl_2]^{5-}$ cluster in the KCl host lattice using ab initio methods, with all possibilities for complexes tested in the energy minimization process. The present results include the unpaired electron orbital symmetry, isotropic hyperfine couplings, quadrupolar interactions, geometry, and total energy. The $[NiCl_6]^{5-}$ cluster was calculated in KCl and NaCl host lattices to analyze the chlorines coordination affinity to Ni(I).

In the last 15 years, progress has been attained in the theoretical model, concerning the representation of the crystalline environments[11−17] for different purposes, as for example, in the calculation of electronic spectroscopy and hyperfine interactions in ionic impure crystals.[10,18] In this direction, embedded cluster calculations (ECC)[10−22] proved to be an important tool in the determination of electronic structure and properties for systems in crystals where a precise wave function is needed in a localized spatial region. For this purpose, total ion potentials (TIP)[15,16] may be used to take into account short-range interactions, and Evjen point charge procedure[23] may be used to take into account the long-range interactions. In particular, accurate geometry of molecular impurities in crystal host lattices, not achievable by X-ray diffraction spectroscopy or by other experimental methods, have been obtained by such methodology.[10,16−18]

In what concerns the calculation and interpretation of hyperfine coupling for gas-phase isolated radicals,[24−27] and for ionic impure crystals,[10,17,18] it has been revealed the importance of spin-polarization and correlation effects. For this purpose, unrestricted Hartree−Fock (UHF) and Møller−Plesset perturbation theory[28] based on ab initio unrestricted spin Hartree−Fock (UMP2)[26,29] has provided theoretical results in excellent agreement with the EPR experiments.[10,17,18,26] In general, other post Hartree−Fock methods, as for example the coupled cluster method, are much more computer consuming and do not provide significant improvements for the A_{iso} calculations.[27] We did not use density functional methods because Eriksson et al. have shown a dependence between the calculated A_{iso} values and the functional forms.[30]

Previous experimental works suggest that the nature of the coordination bonds of coordination compounds are independent of the host lattice and that the distance between metal and CN^- is affected by the ionic interactions with the crystal.[31] This hypothesis was reinforced by recent theoretical results for planar complex $[Ni(CN)_4]^{3-}$ in NaCl and KCl host lattices.[10] Also, the electric field generated at the complex by a host lattice influences the splitting of the central Ni atom d orbitals as well

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* To whom correspondence should be addressed. E-mail: amaral@if.ufrj.br.
[†] Instituto de Física.
[‡] Instituto de Química.

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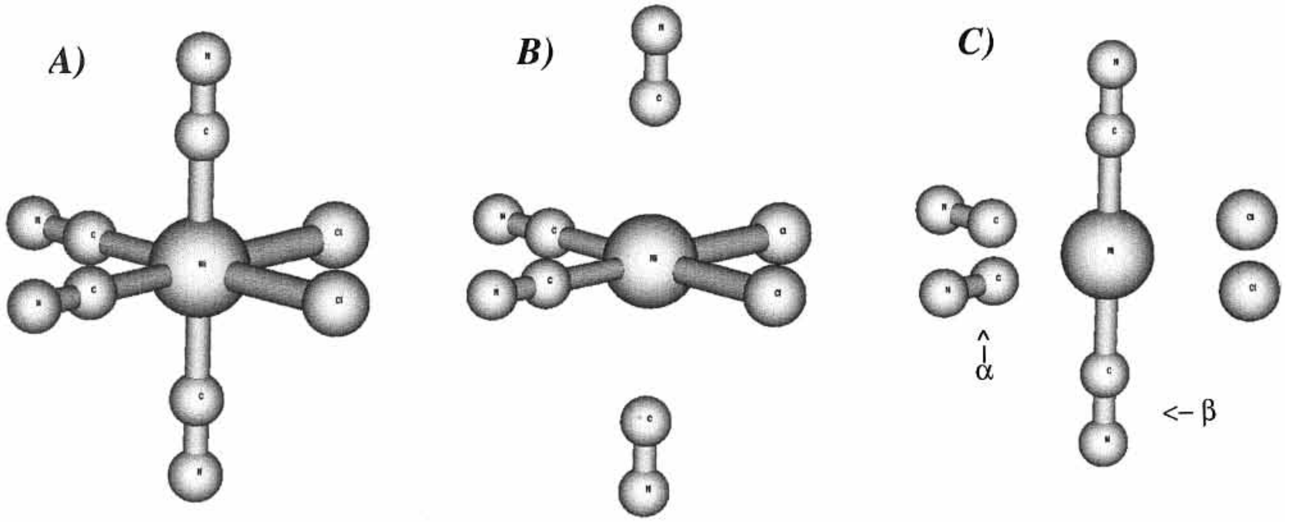

Figure 1. Three possibilities to complex in *cis*-$[Ni(CN)_4Cl_2]^{5-}$ cluster. (A) hexacoordinated *cis*-$[Ni(CN)_4Cl_2]^{5-}$ complex; (B) planar *cis*-$[Ni(CN)_2Cl_2]^{3-}$ complex; (C) linear $[Ni(CN)_2]^{-}$ complex with the two types of cyanides identified as α and β.

as the CN^- ligands orbitals. The dopand $[Ni(CN)_4Cl_2]^{5-}$ cluster, at cis or trans conformation, in KCl host lattice has two Cl^- ions first neighbors of Ni atom. For the square planar complex ESEEM experiments showed hyperfine interactions with the nuclei of these anions but the calculations indicate these anions as host Cl^-. The degree of participation of these host ions on the molecular structure of the *cis*-$[Ni(CN)_4]^{3-}$ complex is investigated in this work by using the geometry and quadrupolar tensor calculated for Cl nuclei. The distances Ni−Cl and Ni−CN and the total energy were compared with those calculated for the *trans*-$[Ni(CN)_4Cl_2]^{5-}$ cluster in order to analyze the structure and stability of the cis complex.

Direct comparison between theoretical and experimental data was made for isotropic magnetic hyperfine couplings (A_{iso}). It was possible to perform a qualitative comparison between the calculated ground state and the measured *g*-tensor, because this tensor is related to the symmetry of the unpaired electron wave function.[5−10] The present theoretical results, besides confirming the unpaired electron orbital assignment and providing precise localization of cyanides and axial host chlorines, are in good qualitative agreement with the measured properties.

We will show that the calculated properties, put together with the EPR experimental data[8] for *cis*-$[Ni(CN)_4Cl_2]^{5-}$ cluster and the available theoretical data on square planar $[Ni(CN)_4]^{3-}$ complex,[10] strongly suggests the formation of a linear Ni(I) complex.

Theoretical Methods

The methodology used in this work was very similar to that described in the previous paper.[10] The system under study is represented by a *cis*-$[Ni(CN)_4Cl_2]^{5-}$ cluster, added by 18 total ion potentials (TIP)[15,16] representing the surrounding K^+ ions, as shown in Figure 2, and by 1306 point charges[23] representing the rest of the crystal. A 6-31+G* Gaussian basis set was used for the N, C, and Cl atoms, and a LanL2DZ[32] basis set was used for the Ni atom. This basis includes polarization and diffuse functions, needed to properly describe delocalized valence electrons of the complex bonding. The 18 electrons of K^+ ions that surround the *cis*-$[Ni(CN)_4Cl_2]^{5-}$ cluster are represented by effective core potentials[32] for the core of K neutral atoms. They take into account the short-range potentials acting on the quantum-mechanical cluster due to the crystal environment. The long-range Coulombic potential of the infinite crystal was considered through point charges. The point charges and TIPs are placed in positions corresponding to pure crystal lattices. With the cluster, the TIPs, and the point charges, it establishes a cube with an edge composed by 11 point charges. At the borders of the cube, ionic fractional charges were used following the Evjen procedure[23] in order to increase convergence of the Madelung potential at the cluster and to preserve system neutrality. The $[NiCl_6]^{5-}$ cluster in KCl or NaCl host lattices was calculated using the same embedding scheme but now with Na^+ first neighbors to $[NiCl_6]^{5-}$ cluster ions represented by TIPs instead of K^+.

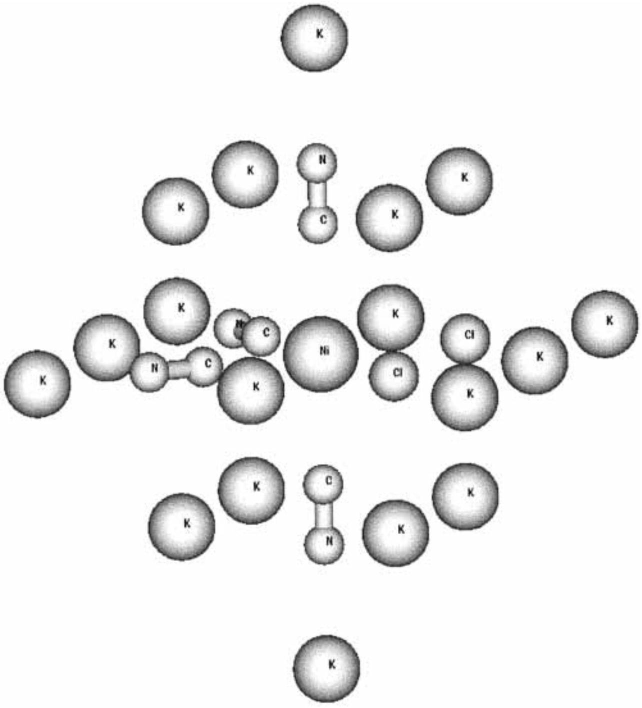

Figure 2. *cis*-$[Ni(CN)_4Cl_2]^{5-}$ cluster plus K^+ PITs used in ab initio calculations.

Within this embedded cluster ambient, the electronic structure and the optimal geometry of the complex were determined by UMP2 calculations using all valence and virtual orbitals. The distance C−N was kept[33] as 1.15, and the Ni−C and Ni−Cl distances were optimized. Positions of TIPs and point charges were kept constant. In these calculations, the hyperfine quadrupolar and magnetic interactions were also determined.

We used the Gaussian 94 program[34] to perform the calculations presented in this work.

The A_{iso} couplings were obtained using the following expression:

$$A_{iso} = (8\pi/3) g \beta g_N \beta_N \rho(N)$$

where $\rho(N)$ is the evaluated spin density[26,27] at the nucleus N, g_N and g are the nuclear and electronic g-factors respectively, β is the Bohr magneton, and β_N is the nuclear magneton.

To analyze the distinct contributions to the hyperfine interactions, restricted open-shell Hartree−Fock (ROHF) and unrestricted spin Hartree−Fock (UHF) wave functions were calculated at the equilibrium geometry.

The hyperfine quadrupolar coupling tensor was obtained from the expression[25]

$$P_{N,i} = \frac{eQ_N EFG_{N,i}}{2I_N(2I_N - 1)}$$

Where e, I_N, Q_N, and $EFG_{N,i}$ are respectively the electron charge, the nuclear spin, the nuclear quadrupole momentum, and the electric field gradient at nucleus N. Index i denotes x, y, or z components.

Results and Discussion

The $\langle S^2 \rangle$ values for the calculated UHF wave functions are 0.7609, and the $\langle S^2 \rangle$ values for the UMP2 wave functions are 0.7564. These $\langle S^2 \rangle$ values, close to the correct value 0.75, indicate a very small influence of the spin contamination in the calculated properties.[29]

The calculated total energy for *cis*-$[Ni(CN)_4Cl_2]^{5-}$ is 0.3 eV higher than the total energy for the *trans*-$[Ni(CN)_4Cl_2]^{5-}$ cluster. In other words, conformation trans, the square planar complex, is more stable than the cis conformation for the $[Ni(CN)_4Cl_2]^{5-}$ cluster.

From now on, we will discuss the different results related to the *cis*-$[Ni(CN)_4Cl_2]^{5-}$ UMP2 embedded cluster calculations compared with the experimental results.[8] We will designate the cyanides in the Cl−Ni−Cl plane as α and the cyanides orthogonal to this plane as β, as indicated in Figure 1C. The following reasoning clearly indicates the presence of the linear $[Ni(CN)_2]^-$ complex.

(1) In what concerns the nature of the bonding between the α cyanides and the Ni atom (localized in the Cl−Ni−Cl plane), the calculated electronic structure assigns A_1 symmetry to the unpaired electron orbital, with a predominant $d_{x^2-y^2}$ character, in agreement with the measured g values ($g_x = 2.132$, $g_y = 2.231$, and $g_z = 2.010$).[8] Figure 3 shows that nodes between the Ni atom and the cyanide ligands ascribe this orbital an antibonding character. Symmetry allows participation of p_x and p_y basis functions in the unpaired electron orbital, as previously inferred from the measured g-tensor components.[8]

(2) The Ni−C_α calculated distance is longer than the Ni−C distance in the square planar complex, whereas the Ni−C_β distance is shorter (Table 2). There are two bond orders in the *cis*-$[Ni(CN)_4Cl_2]^{5-}$ cluster, one smaller than square planar for α cyanides and one larger for β cyanides. In other words, the theoretical results, 1 and 2, suggest no coordination between α cyanides and the Ni atom.

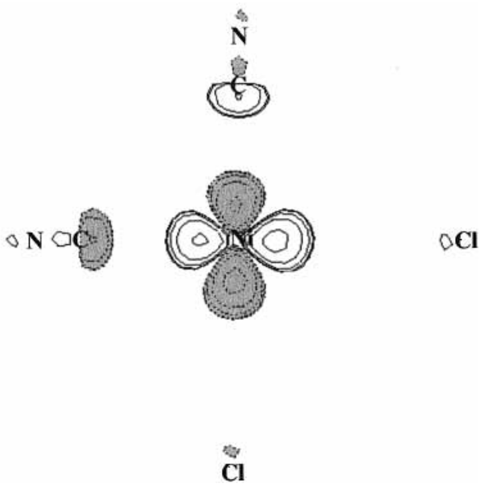

Figure 3. *cis*-$[Ni(CN)_4Cl_2]^{5-}$ cluster unpaired electron molecular orbital.

TABLE 1: Calculated (UMP2 Method) Distances in the Clusters *trans*-$[Ni(CN)_4Cl_2]^{5-}$ and *cis*-$[Ni(CN)_4Cl_2]^{5-}$ (Å)

	cluster	
distance	*cis*-$[Ni(CN)_4]^{3-}$	*trans*-$[Ni(CN)_4]^{3-}$ [a]
Ni−C_α	2.26	2.11
Ni−C_β	2.01	
Ni−Cl	3.20	3.23
Cl pure crystal[b]	3.15	

[a] Reference 10. [b] Reference 35.

TABLE 2: A_{iso} Values for *cis*-$[Ni(CN)_4Cl_2]^{5-}$ Cluster (MHz)

nucleus	theory	exp[a]
$^{13}C_\alpha$	34.7	42.0
$^{13}C_\beta$	11.4	21.0
$^{14}N_\alpha$	2.7	
$^{14}N_\beta$	5.0	
^{35}Cl	5.8	small unresolved

[a] Reference 8.

(3) The interpretation of the poorly resolved CW-EPR spectrum recognizes two types of cyanides, with 42 and 21 MHz ^{13}C A_{iso} values.[8] These values must be regarded as semiquantitative information because of the difficulty in evaluating complex ^{13}C A_{iso} arising from partially enriched samples (70% ^{13}C) with four carbon atoms per complex. Our present theoretical results, as shown in Table 2, also contemplate two types of cyanides, 34.7 and 11.4 MHz, for the ^{13}C A_{iso} values respectively for the α and β cyanides. In the α cyanides, ^{13}C A_{iso} arises from direct contribution of the unpaired electron antibonding orbital and also from spin polarization of CN^- valence orbitals.[10,18] In β cyanides, ^{13}C A_{iso} arises only from spin polarization of $[Ni(CN)_2]^-$ linear complex molecular orbitals because symmetry demands a null direct spin density at C_β−Ni−C_β axes.

(4) The calculations also indicate no covalent bonding between the metal and the first neighbors Cl atoms, first by considering the nonbonding character of the molecular orbitals localized on Cl ions, second because the calculated Mulliken charge on Chlorine atoms is −0.90, similarly to the *trans*-$[Ni(CN)_4Cl_2]^{5-}$ cluster,[10] and third because the calculated distances between Ni and Cl nuclei are close to the perfect crystal lattice constant (Table 2), reinforcing that Cl ions are host lattice anions. Finally, the small values for the calculated quadrupolar interactions ($P_x = -0.13$; $P_y = -0.07$; $P_z = 0.20$) indicate near cubic symmetry around these nuclei, as expected for host chlorines. These quadrupolar components are even smaller than those calculated for Cl nuclei as first neighbors to Ni in a square planar complex.[10] The small Cl A_{iso} value arises

TABLE 3: Calculated Distances in $[NiCl_6]^{5-}$ Cluster in KCl or NaCl Host Lattices (MHz)[a]

	KCl	NaCl
$NiCl_{ax}$	3.03	2.78
$NiCl_{eq}$	2.84	2.65
distance in pure crystal[b]	3.14	2.82

[a] ax = axial; eq = quatorial. [b] Reference 35.

mainly from spin polarization, because these spherical ions are far away from the Ni atom. Our calculations on the $[KCl_6]^{5+}$ and $[NaCl_6]^{5+}$ embedded clusters show that optimized geometry is obtained when chlorines first neighbors are near the lattice positions (Table 3), confirming the chlorine preference to be a host ion.

These facts and the idea that chlorines first neighbors to Ni are host ions strongly suggests a $[NC-Ni-CN]^-$ complex (Figure 1C) instead of a *cis*-$[Ni(CN)_4Cl_2]^{5-}$ complex (Figure 1A). The other two cyanides do not behave as ligand ions, being submitted only to an electrostatic potential. Usually reported Ni(I) coordinations are planar[1−10] or sometimes pentacoordinated.[5−7] Formation of a linear complex requires a special situation. As the original dopand in KCl lattice is a planar $[Ni(CN)_4]^{2-}$ complex, the fcc host structure imposes two chlorine first neighbors to Ni. Reduction of this diamagnetic complex results in a d^9 paramagnetic *trans*-$[Ni(CN)_4]^{3-}$ complex.

However, energy transfer from 2 Mev electron radiation may provide formation of a *cis*-$[Ni(CN)_4Cl_2]^{5-}$ cluster. The system has now two options: two cyanide ligands in the antibonding unpaired electron orbital plane or two cyanide ligands in the axis orthogonal to the unpaired electron orbital. The second option is the most stable because the coordination bonds are not destabilized by the unpaired electron, thus forming the exotic linear $[Ni(CN)_2]^-$ complex.

Conclusions

In this work, we performed embedded cluster ab initio UMP2 calculations for $[Ni(CN)_4Cl_2]^{5-}$ cluster in cubic KCl host lattice.

The calculated final symmetry for the electronic wave function, A_1, agrees with the experimental predictions inferred from the *g*-tensor. UHF calculations indicate that the unpaired electron lies basically in a Ni $d_{x^2-y^2}$ orbital, with antibonding character.

The calculated quadrupolar tensor and position of Cl nuclei show that clorine ions first neighbors to Ni are not coordinated to this atom. The calculations agree with experiments identifying two distinct pairs of equivalent cyanides by geometry and A_{iso} values. The theoretical results suggest that two cyanides, pointing to $d_{x^2-y^2}$ unpaired electron orbital, are not ligands to central Ni. The final picture to the $[Ni(CN)_4Cl_2]^{5-}$ cluster in cubic KCl host lattice is formed to the linear $[Ni(CN)_2]^-$ complex interacting with two CN^- and two Cl^- ions despite the preceding interpretation that suggest the $[Ni(CN)_4Cl_2]^{5-}$ complex.

The electronic structure calculated by the embedded cluster UMP2 method shows a picture in complete agreement with the experimental results. In this sense, we believe that the approximations, Evjen for long-range lattice interactions and TIPs for short-range lattice interaction and frozen lattice ions positions, can be used to predict geometrical distortions on complexes inserted in ionic host lattices and to interpret the bonding character between the cyanides or chlorines and the Ni atom.

References and Notes

(1) Zotti, G.; Pilloni, G.; Rigo, P.; Martelli, M. *J. Electroanal. Chem.* **1981**, *124*, 177.

(2) Furenlid, L.; Renner, M.; Fujita, E. *Physica B* **1995**, *208*, 739.

(3) Kaasjager, V. E.; Puglisi, L.; Bouwman, E.; Driessen, W. L.; Reedijk, J.; *Inorg. Chim. Acta* **2000**, *310*, 183.

(4) Fox, S.; Stibrany, R. T.; Potenza, J.; Shugar, H. *Inorg. Chim. Acta* **2001**, *316*, 122.

(5) Lepetit, C.; Kermarec, M.; Che, M.; Thomas, J. M. *Colloids Surf., A* **1993**, *72*, 265.

(6) Lepetit, C.; Kermarec, M.; Olivier D. *J. Mol. Catal.* **1989**, *51*, 73.

(7) Lepetit, C.; Kermarec, M.; Olivier D. *J. Mol. Catal.* **1989**, *51*, 95.

(8) Zanette, S. I.; Caride, A. O.; Danon, J. *J. Chem. Phys.* **1976**, *64*, 3381.

(9) Jain, S. C.; Reddy, K. V.; Gupta, C. L.; Reddy, T. Rs. *Chem. Phys. Lett.* **1973**, *21*, 150.

(10) Leitão, A. A.; Coelho Neto, J. A.; Pinhal, N. M.; Bielschowsky, C. E.; Vugman, N. V. *J. Phys. Chem. A* **2001**, *105*, 614.

(11) Sousa, C.; Casanovas, J.; Rubio, J.; Illas, F. *J. Comput. Chem.* **1993**, *14*, 680.

(12) Aachi, J.-I.; Kosugui, N. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 3314.

(13) Miyoshi, E.; Miyake, Y.; Katsuki, S.; Sakai, Y. *J. Mol. Struct. (THEOCHEM)* **1998**, *451*, 81.

(14) Berrondo, M.; Rivas-Silva, J. F. *Int. J. Quantum Chem.* **1995**, *29*, 253.

(15) Winter, N. W.; Pitzer, R. M.; Temple, D. K. *J. Chem. Phys.* **1987**, *87*, 2945.

(16) Winter, N. W.; Pitzer, R. M.; Temple, D. K. *J. Chem. Phys.* **1987**, *86*, 3549.

(17) Leitão, A. A.; Capaz, R. B.; Vugman, N. V.; Bielschowsky, C. E. *J. Mol. Struct. (THEOCHEM)* **2002**, *580*, 65.

(18) Leitão, A. A.; Vugman, N. V.; Bielschowsky, C. E. *Chem. Phys. Lett.* **2000**, *321*, 269.

(19) Ferrari, A. M.; Soave, R.; D′Ercole A.; Pisani C.; Giamello, E.; Pacchioni, G. *Surf. Sci.* **2001**, *479*, 83.

(20) Vail, J. M.; Emberly, E.; Lu, T.; Gu, M.; Pandely, R. *Phys. Rev. B* **1998**, *57*, 764.

(21) Al-Abdalla, A.; Barandiarán, Z.; Seijo, L.; Lindh, R. *J. Chem. Phys.* **1998**, *108*, 2005.

(22) Puchin, A. A. V.; Puchin, V. E.; Kotomin, E. A.; Reichling, M. *Sol. Stat. Comm.* **1998**, *106*, 285.

(23) Evjen, H. M. *Phys. Rev.* **1932**, *39*, 675.

(24) Chipman, D. M.; Carmichael, I.; Feller, D. *J. Phys. Chem.* **1991**, *95*, 4702.

(25) Penner, G. H. *Chem. Phys. Lett.* **1996**, *261*, 665.

(26) Gauld, J. W.; Eriksson, L. A.; Radom, L. *J. Phys. Chem. A* **1997**, *101*, 1352.

(27) Knight, L. B., Jr.; Hill, D.; Berry, K.; Babb, R.; Feller, D. *J. Chem. Phys.* **1996**, *105*, 5672.

(28) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

(29) Chen, W.; Schlegel, H. B. *J. Chem. Phys.* **1994**, *101*, 5957.

(30) Eriksson, L. A.; Malkin, V. G.; Malkina, O. L.; Salahub, D. R. *Int. J. Quantum Chem.* **1994**, *52*, 879.

(31) Vugman, N. V.; Amaral, M. R., Jr. *Phys. Rev. B* **1990**, *42*, 9837.

(32) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270. Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284. Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

(33) Manoharan, P. T.; Gray, H. B. *J. Am. Chem. Soc.* **1965**, *87*, 3340.

(34) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, revision C.3; Gaussian, Inc.: Pittsburgh, PA, 1995.

(35) Harrison, W. A. *Electronic Structure and the Properties of Solids*; Dover Publications, Inc.: New York, 1989; Chapter 8.