4938 J. Phys. Chem. A **2002,** *106,* 4938−4941

Further Theoretical Evidence for the Exceptionally Strong Ferromagnetic Coupling in Oxo-Bridged Cu(II) Dinuclear Complexes

Eliseo Ruiz,*,† Coen de Graaf,‡ Pere Alemany,‡ and Santiago Alvarez†

Centre de Recerca en Química Teòrica (CeRQT), Departament de Química Inorgànica and Departament de Química Física, Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain

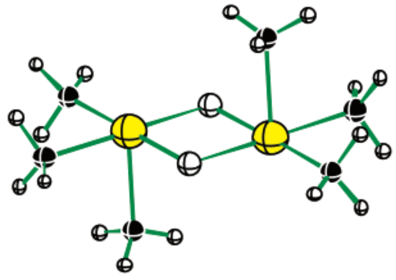
Received: October 15, 2001; In Final Form: February 5, 2002

The magnetic behavior of the oxo-bridged Cu(II) dinuclear complexes has been investigated using hybrid density functional methods (B3LYP) and a post-Hartree−Fock approach (difference-dedicated configuration interaction method, DDCI). Both methods confirm the strong ferromagnetic coupling predicted for such complexes at geometries close to the energy minimum. For large Cu−O−Cu bridging angles, the DFT calculations predict an increase, whereas the DDCI method predicts a decrease of the ferromagnetic interaction, a result that is associated with the different weight of the excited charge-transfer configurations.

Introduction

An important hindrance for the development of the field of molecular magnetism is the scarcity of bridging ligands that favor ferromagnetic coupling in di- or polynuclear transition-metal complexes.[1] For instance, among the Cu(II) dinuclear complexes, probably the most studied family of compounds in this field, only the end-on azido bridging ligand always gives complexes with relatively strong ferromagnetic coupling.[2] Also, the hydroxo-bridged Cu(II) complexes may present ferromagnetic coupling depending on structural parameters such as the Cu−O−Cu bond angle and the out-of-plane shift of the hydrogen atom.[3] These are the only known ligands that usually give strong ferromagnetic coupling among late transition metals. Although the magnetic properties of dinuclear early transition-metal complexes have been less studied, it is also worth mentioning the very strong ferromagnetic coupling in complexes with a single V−O−V bridge.[4]

Recently, we have shown the ability of methods based on density functional theory (DFT)[5,6] to provide good estimates of exchange coupling constants.[3] For this reason, we undertook a computational search of ligands that could lead to new families of transition-metal complexes with ferromagnetic coupling.[7] We analyzed the influence of the substitution of the hydrogen atom at the hydroxo bridging ligand and found that the presence of highly electropositive substituents enhances the ferromagnetic coupling. Therefore, we predicted very strong ferromagnetic coupling for complexes with the −OLi bridge, while the strongest coupling is predicted for the bare oxo ligand. For a model in which the bridging framework structure (**1**) was optimized, we obtained a calculated exchange coupling constant J of $+661$ cm^{-1} (using the Heisenberg Hamiltonian $H = -JS_1S_2$). This value is three times larger than the strongest known coupling in end-on azido Cu(II) dinuclear complexes. Recently, Blanchet-Boiteux and Mouesca have performed a study of oxo-bridged Cu(II) complexes using broken-symmetry DFT calculations and analyzed the magnetic properties through the Kahn−Briat[8,9] valence bond model.[10,11] They concluded that the very strong ferromagnetic coupling that we have predicted for those complexes is linked to an artifact of the broken-symmetry calculations, associated with the presence of a larger copper spin population in the spin-paired broken-symmetry solution than in the triplet state.



1

The aim of this communication is to extend our previous work[7] on the so-far hypothetical oxo-bridged Cu(II) dinuclear complexes by applying the difference-dedicated configuration interaction method (DDCI) and to verify whether the strong coupling predicted by the DFT results is just an artifact of the DFT methodology employed. The DDCI method is specifically designed to determine small energy differences,[12,13] and it is the state-of-the-art among the post-Hartree−Fock approaches to calculate exchange coupling constants.[14−18] The detailed description of the technical aspects of these calculations is included in the Appendix.

Results of DFT Calculations

In our previous work, we performed calculations for models with different coordination numbers for Cu(II), although we did not systematically compare the exchange coupling constants obtained in each case. In Figure 1, we show the dependence of the calculated coupling constant with the Cu−O−Cu bond angle θ (B3LYP method) for model **1**,[19] as well as for analogous models with two or no axial ammonia ligands on each copper atom (i.e., coordination numbers five, six, and four, respectively). In all cases, the ferromagnetic coupling constant increases considerably as the Cu−O−Cu angle increases. Such behavior is markedly different from that found for other families of dinuclear Cu(II) complexes, for which a parabolic dependence

---

† Departament de Química Inorgànica.
‡ Departament de Química Física.

10.1021/jp015565b CCC: $22.00

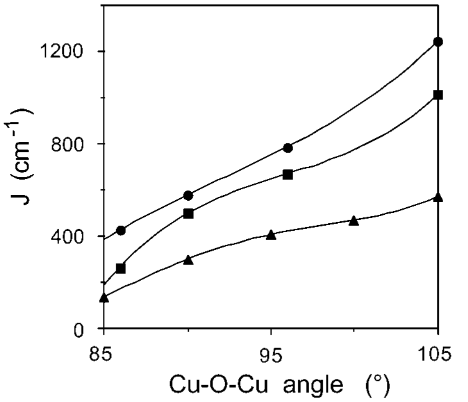


Figure 1. Calculated exchange coupling constant as a function of the Cu−O−Cu angle (double-ζ basis set, B3LYP method) for models with two (▲), one (model **1**, ■), or no axial ammonia ligands (●).[21]

of J on the bridging angle has been found, with a maximum in the range of the bridge angles studied.[2,3,20] The calculated coupling constant J is seen to decrease upon addition of axial ammonia ligands to the model. Such a result is surprising, considering that the orbitals bearing the unpaired electrons are located in the xy plane, whereas the additional ligands are coordinated along the z axis. The influence of the basis set has also been analyzed. The use of a triple-ζ basis set for the copper atoms results in an increase of 10−20% of the calculated coupling constant (results not shown in Figure 1) with respect to the value obtained with a double-ζ basis set but does not change the overall trend observed with the smaller basis.

We are interested in learning whether the DFT results for the oxo-bridged complexes follow the relationship proposed by Hay−Thibeault−Hoffman[22] (eq 1, where K_{ab}, J_{aa}, and J_{ab} are the two-electron integrals involving the two orbitals localized on each metal center).

$$J = 2K_{ab} - \frac{(\epsilon_1 - \epsilon_2)^2}{J_{aa} - J_{ab}} \tag{1}$$

The representation of J as function of the square of the eigenvalue gap, $(\epsilon_1 - \epsilon_2)^2$, indicates that larger values of the energy gap correspond to weaker ferromagnetic coupling as expected from eq 1. However, the relationship between the two magnitudes is far from linear (linear regression coefficient 0.70). This fact seems to be a general feature of systems with a near degeneracy of the orbitals containing the unpaired electrons, as reported previously for the 1,3-azido-bridged ligands.[23] In such cases, there is a subtle interplay between the two- and one-electron contributions in eq 1, and small changes in the energy gap can produce very important changes in the antiferromagnetic contribution (second term in eq 1).

DDCI Results

In Figure 2, we show the dependence of the exchange coupling constant on the Cu−O−Cu angle for model **1**, as calculated with the DDCI method. Comparison of the B3LYP and DDCI results (Figures 1 and 2) shows that the expected behavior at angles smaller than 95° is similar in both cases: the ferromagnetic exchange is enhanced as the Cu−O−Cu angle increases. However, the two methods differ in their predictions for angles between 95° and 105°. We note also that in recent studies using the B3LYP method,[24] we found for several families of dinuclear Cu(II) complexes a parabolic dependence of J on the bridging angle, as found here when the DDCI method is applied to the oxo-bridged complexes. Hence, the B3LYP results obtained for bridging angles larger than 95° seem to be anomalous by comparison both with the DDCI results on the same system and with the B3LYP results on compounds with other bridges.

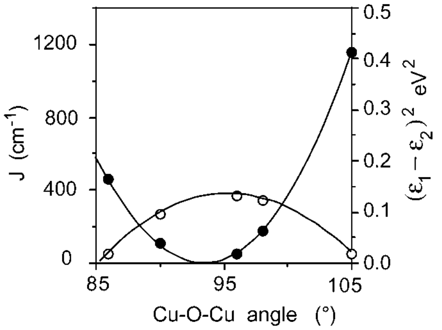


Figure 2. Exchange coupling constant (○) and square of the energy difference between the two orbitals bearing the unpaired electrons (●) as a function of the Cu−O−Cu angle, as calculated for model **1** with the DDCI method.

The energy minimum of the triplet state appears at around 90° for this model, indicating that structures with a strong ferromagnetic coupling can be expected for this kind of complexes. Such an angle is practically coincident with that obtained using the B3LYP method (91°). The analysis of the eigenvalues corresponding to the orbitals with the unpaired electrons reveals that the smallest energy gap corresponds to the largest exchange coupling constant, although the correlation expected from the Hay−Thibeault−Hoffmann model (eq 1) is not found (linear regression coefficient 0.65).

Analysis of the Spin Density

In a recent work, Blanchet-Boiteux and Mouesca[10,11] suggested that the anomalous dependence of J on the bond angle in our previous B3LYP calculations could be ascribed to the presence of a larger copper spin population in the broken-symmetry solution than in the triplet state. They propose that the antiferromagnetic part of the exchange coupling constant can be split in two terms, one associated with the metal d orbitals that is always positive and a second term representing the contribution of the bridging ligand. This second term may be negative and can be related to the copper spin population through an analytical expression (eq 2) derived from a Mulliken population analysis.

$$J_{bdg} \propto -(\rho_{HS}^{\ 2} - \rho_{BS}^{\ 2}) \tag{2}$$

Thus, if the copper spin population in the broken-symmetry solution is larger than that in the triplet state, J_{bdg} turns out to be positive. These authors suggest that the origin of the strong ferromagnetic coupling could originate from this fact because in such conditions all of the contributions to the coupling constant would be positive. It is worth noting that eq 2 and a similar expression proposed by us introducing the orbital overlap between the two localized broken-symmetry orbitals[25] are only applicable when this overlap is very small. As shown in ref 11, this overlap increases considerably for large Cu−O−Cu angles and, consequently, the results obtained with these expressions must be considered carefully for the oxo-bridged Cu(II) complexes.

To further check whether the differences between the B3LYP and DDCI results are associated with the larger copper spin population of the broken-symmetry solution, we have analyzed

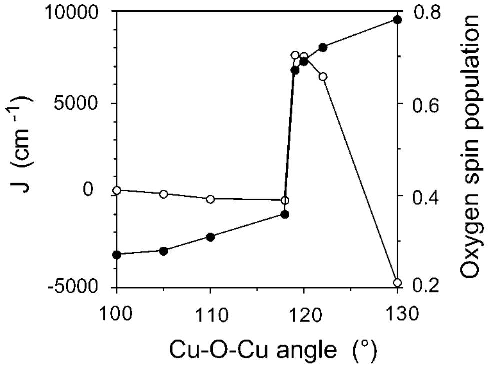


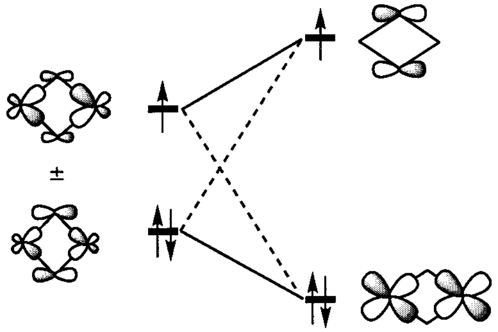
Figure 3. Exchange coupling constant (○) and oxygen spin population for the triplet state (●) calculated with the DDCI method for model **1** at large bridging angles.

the spin-density distribution calculated with the two methods. We observe that for the model with hexacoordinated metal atoms the copper spin densities in the two states are in the right order, $\rho_{HS} > \rho_{BS}$, and still abnormally high positive values of J are calculated at large Cu−O−Cu bond angles. If we employ a more accurate procedure to estimate such spin populations, such as the NBO approach (where NBO stands for natural bond orbital) instead of the Mulliken population analysis, the copper spin population is larger in the triplet state for the three models. Thus, the difference between the copper spin populations calculated for the broken-symmetry and triplet states cannot account, at least in this case, for the anomalous dependence of J on the bond angle found with the B3LYP calculations.

The major discrepancy between our B3LYP and DDCI calculations is the large spin population found at the oxygen atoms with the former method at large Cu−O−Cu angles. For the model without axial ligands at a Cu−O−Cu angle of 105°, the NBO−B3LYP calculations indicate that a large portion of the spin population is located at the bridging oxygen (0.56) rather than at the copper atoms (0.40), while the spin populations obtained with the DDCI method are still mostly localized at the copper atoms (0.28 and 0.66 for oxygen and copper, respectively). Our B3LYP results are in agreement with those of Blanchet-Boiteux and Mouesca,[11] who also obtain large spin populations for the oxygen atoms by using nonhybrid functionals. At larger angles, however, even the DDCI calculations (Figure 3) show a progressive localization of the spin density onto the oxygen atoms, with an abrupt increase close to 120°. In essence, thus, the two methods predict localization of the unpaired electrons at the oxygen atoms for large angles, combined with a very strong ferromagnetic coupling, the main difference being the angle at which this phenomenon becomes evident and the abruptness of the change in spin localization. It must be stressed though, that these discrepancies arise only for geometries that are far from the energy minimum, whereas there is good agreement in the region near the minimum.

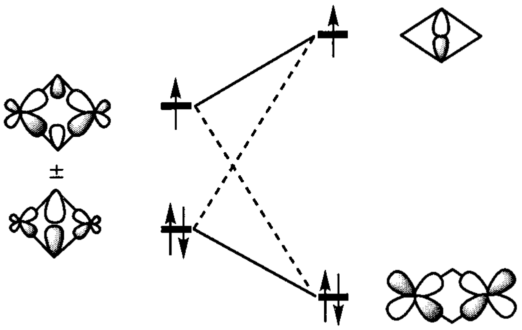
The analysis of the DDCI wave functions shows that there are four states involved. First, there are two $S = 0$ states: one is an open-shell singlet and appears at small angles, and the second one is a closed-shell state that becomes more stable at bridging angles larger than 119°. We have also detected sizable contributions from two triplet states: the first one is the ground state at small angles and shows the spin population located at the copper atoms, while a second triplet has the spin density located mainly at the oxygen atoms and is reflected in the abrupt change of the spin population shown in Figure 3.

As the angle is increased, the two oxo bridges approach each other. As a result, one of the singly occupied molecular orbitals (SOMO), of Cu−O σ^* character but O−O π^* in nature, gradually loses its majoritary metal d contribution by mixing with the bonding orbital of the same symmetry, as schematically shown in **2**. A similar situation occurs with the other SOMO,



2

incorporating now O−O σ^* character (**3**). At a large enough

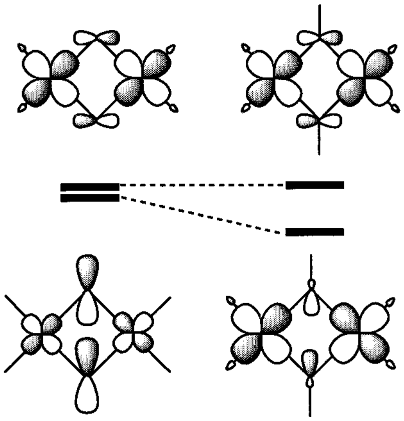


3

angle, the electron in the σ^* orbital would be transferred to the π^* one, thus accounting for the formation of a peroxo bridge. The formation of a peroxo bridge at large bond angles was previously proposed by Blanchet-Boiteux and Mouesca.[11] The important change in the energy of these four orbitals with the O−Cu−O bond angle results in a variety of configurations within the 3d manifold with similar energies that give rise to several triplets and singlets of the same symmetry (B_{1u}). It is clear that the DDCI method is best suited to adequately handle the extensive configuration interaction that appears at intermediate angles. The abrupt change in J and spin populations at ca. 120° thus corresponds to a triplet transition state in the oxo/Cu(II) to peroxo/Cu(I) transformation in which two electrons have been already transferred from the oxygen to the copper atoms.

Conclusions

We have seen that both methods, B3LYP and DDCI, indicate that the energy minimum for the oxo-bridged complexes is very close to the ideal prototype situation proposed by Goodenough and Kanamori[26−28] for ferromagnetic coupling: a Cu−O−Cu bridging angle close to 90°, and an oxo bridging ligand without substituents. The first condition is fulfilled usually only by the oxo-bridging ligands, because the inclusion of substituents bonded to the bridging oxygen atoms results in a shift of the mimimum to larger Cu−O−Cu angles. For instance, when the B3LYP method is used for the hydroxo- and alkoxo-bridged Cu(II) complexes, the Cu−O−Cu angles corresponding to the energy minimum are 102° and 103°, respectively, when the substituent is within the Cu_2O_2 framework plane. The second point is very important for the ferromagnetic coupling because the presence of a substituent at the bridging oxygen, such as the hydrogen atom in the hydroxo-bridged complexes, breaks the almost perfect orbital degeneracy that we have found for the oxo-bridged complexes (**4**). The B3LYP calculations for a bridging angle of 96° tell us that interaction with the hydrogen atom results in a hybridization and stabilization of the oxygen p_z orbital, thus weakening the interaction with the metal d orbitals and making the SOMO less antibonding. The outcome is an increased gap and an enhanced antiferromagnetic contribution. Despite the simplicity of the structural models employed, these results using the DDCI method confirm our previous predictions about the strong ferromagnetic coupling in the oxo-bridged complexes.



4

Acknowledgment. Our work was supported by DGES through Project PB98-1166-C02-01. Additional support came from CIRIT through Grant SGR99-0046. The computing resources were generously made available in the Centre de Supercomputació de Catalunya (CESCA) with a grant provided by Fundació Catalana per a la Recerca (FCR) and the Universitat de Barcelona.

Appendix: Computational Details

The DFT calculations were carried out using the B3LYP functional[29−31] as implemented in the Gaussian package.[32] A double-ζ basis set was employed for main group elements and double-ζ[33] and triple-ζ basis sets[34] were employed for the copper atom. The calculations of the exchange coupling constants were performed using a modified broken-symmetry approach in which the energy corresponding to the broken-symmetry wave function is not projected.[25] The DDCI calculations were done by means of the CASDI code,[35,36] using the starting orbitals generated with the MOLCAS 5 package.[37] An ANO-type basis set[38,39] was employed with the following contractions: Cu(5s,4p,3d), O(4s,3p), N(3s,2p), and H(2s). The DDCI space was selected by including the following valence orbitals: 3d for Cu, 2s and 2p for O, 2s and 2p for N, and 1s for H.

References and Notes

(1) Kahn, O. *Molecular Magnetism*; VCH Publishers: New York, 1993.

(2) Ruiz, E.; Cano, J.; Alvarez, S.; Alemany, P. *J. Am. Chem. Soc.* **1998**, *120*, 11122.

(3) Ruiz, E.; Alemany, P.; Alvarez, S.; Cano, J. *J. Am. Chem. Soc.* **1997**, *119*, 1297.

(4) Grant, M. C.; Stamper, B. J.; Knapp, M. J.; Folting, K.; Huffman, J. C.; Hendrickson, D. N.; Christou, G. *J. Chem. Soc., Dalton Trans.* **1999**, 3399.

(5) Parr, R. G.; Yang, W. *Density-Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989.

(6) Koch, W.; Holthausen, M. C. *A Chemist's Guide to Density Functional Theory*; Wiley-VCH Verlag: Weinheim, Germany, 2000.

(7) Ruiz, E.; Alvarez, S.; Alemany, P. *Chem. Commun.* **1998**, 2767.

(8) Kahn, O.; Briat, B. *J. Chem. Soc. Trans.* **1976**, *72*, 1441.

(9) Kahn, O.; Briat, B. *J. Chem. Soc. Trans.* **1976**, *72*, 268.

(10) Blanchet-Boiteux, C.; Mouesca, J. M. *Theor. Chem. Acc.* **2000**, *104*, 257.

(11) Blanchet-Boiteux, C.; Mouesca, J. M. *J. Phys. Chem. A* **2000**, *104*, 2091.

(12) Miralles, J.; Daudey, J. P.; Caballol, R. *Chem. Phys. Lett.* **1992**, *198*, 555.

(13) Miralles, J.; Castell, O.; Caballol, R.; Malrieu, J. P. *Chem. Phys.* **1993**, *172*, 33.

(14) Moreira, I. de P. R.; Illas, F.; Calzado, C. J.; Sanz, J. F.; Malrieu, J. P.; Ben Amor, N.; Maynau, D. *Phys. Rev. B* **1999**, *59*, R6593.

(15) Calzado, C. J.; Malrieu, J.-P.; Cabrero, J.; Caballol, R. *J. Phys. Chem. A* **2000**, *104*, 1579.

(16) Cabrero, J.; Ben-Amor, N.; de Graaf, C.; Illas, F.; Caballol, R. *J. Phys. Chem. A* **2000**, *104*, 9983.

(17) Muñoz, D.; Illas, F.; Moreira, I. de P. R. *Phys. Rev. Lett.* **2000**, *84*, 1579.

(18) Calzado, C. J.; Cabrero, J.; Malrieu, J.-P. *J. Chem. Phys.* **2002**, *116*, 2727.

(19) The following structural parameters were used for the model calculations: Cu−O = 1.94 Å; $Cu-N_{eq}$ = 92.90 Å; $Cu-N_{ax}$ = 92.25 Å; N−H = 91.90 Å; N−Cu−N = 83°; Cu−N−H = 109.105°.

(20) Ruiz, E.; Alemany, P.; Alvarez, S.; Cano, J. *Inorg. Chem.* **1997**, *36*, 3683.

(21) The different results obtained for this model in comparison with our previous paper (ref 7) are the due to the use of a more realistic N−Cu−N bond angle.

(22) Hay, P. J.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1975**, *97*, 4884.

(23) Fabrizi de Biani, F.; Ruiz, E.; Cano, J.; Novoa, J. J.; Alvarez, S. *Inorg. Chem.* **2000**, *39*, 3221.

(24) Ruiz, E.; Alvarez, S.; Rodríguez-Fortea, A.; Alemany, P.; Pouillon, Y.; Massobrio, C. In *Magnetism: Molecules to Materials II*; Miller, J. S., Drillon, M., Eds.; Wiley-VCH: New York, 2001; pp 227−279.

(25) Ruiz, E.; Cano, J.; Alvarez, S.; Alemany, P. *J. Comput. Chem.* **1999**, *20*, 1391.

(26) Goodenough, J. B. *Phys. Rev.* **1955**, *100*, 564.

(27) Goodenough, J. B. *Magnetism and Chemical Bond*; Interscience: New York, 1963.

(28) Kanamori, J. *J. Phys. Chem. Solids* **1959**, *10*, 87.

(29) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(30) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(31) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(32) 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 E.1; Gaussian, Inc.: Pittsburgh, PA, 1995.

(33) Schaefer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571.

(34) Schaefer, A.; Huber, C.; Ahlrichs, R. *J. Chem. Phys.* **1994**, *100*, 5829.

(35) Maynau, D.; Ben-Amor, N., *CASDI*; Université Paul Sabatier: Toulouse, France, 1997.

(36) Ben-Amor, N.; Maynau, D. *Chem. Phys. Lett.* **1998**, *286*, 211.

(37) Andersson, K.; Barysz, M.; Bernhardsson, M. R.; Blomberg, M. R. A.; Cooper, D. L.; Fleig, T.; Fülscher, M. P.; de Graaf, C.; Hess, B. A.; Karlström, G.; Lindh, R.; Malmqvist, P.-Å.; Neogrády, P.; Olsen, J.; Roos, B. O.; Schimmelpfennig, B.; Schütz, M.; Seijo, L.; Serrano-Andrés, L.; Siegbahn, P. E. M.; Stårling, J.; Thorsteinsson, T.; Veryazov, V.; Widmark, P.-O. *Molcas5.0*; Lund University: Lund, Sweden, 2000.

(38) Widmark, P.-O.; Malmqvist, P.-Å.; Roos, B. O. *Theor. Chim. Acta* **1990**, *77*, 291.

(39) Pou-Amérigo, R.; Merchán, M.; Nebot-Gil, I.; Widmark, P.-O.; Roos, B. O. *Theor. Chim. Acta* **1995**, *92*, 149.