



First principles studies of the electronic and magnetic structures of $[\text{Fe}(\text{pz})_2]_x$ complex

L. Kabalan, S.F. Matar *

Université de Bordeaux, CNRS, ICMCB, 87 Avenue du Dr. Albert Schweitzer, F-33608 Pessac Cedex, France

ARTICLE INFO

Article history:

Received 23 December 2008

Accepted 18 February 2009

Available online 4 March 2009

This paper is dedicated to the memory of Professor Olivier Kahn.

Keywords:

DFT

Exchange parameters

Antiferromagnets

Gaussian03

IR

Raman

ASW

ABSTRACT

Polybis(pyrazolato)iron(II), $[\text{Fe}(\text{pz})_2]_x$ is characterized by doubly bridged iron with pyrazolate ligands. An original DFT study at both the molecular and extended solid levels is carried out for this complex system with the purpose of identifying the magnetic interactions and chemical bonding characteristics. From molecular calculations, the exchange parameter J is obtained, pointing to the expected weakly antiferromagnetic ground state. The IR and Raman spectra have been calculated with relevant assignments, namely for the stretching modes. Computations for the extended solid in different magnetic configurations point to the total moment of $4\mu_B \cdot \text{fu}^{-1}$, identifying Fe as divalent in high spin configuration, in accordance with a weak tetrahedral crystal field. From relative energies the ground state is antiferromagnetic. Analyses of the chemical bonding (COOP) and of electron localization function (ELF) illustrate the interactions between Fe and the cycle as well as within the pz cycle.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

In recent years, there has been a growing interest in preparing and characterizing “molecular materials” such as coordination systems for their possible application in a number of different fields [1]; indeed some metal-containing coordination species have been shown to be photo-chemically active or to possess interesting electrical, electrochemical, magnetic properties and even antimicrobial activity [2]. Such systems typically contain a backbone of transition metal ions in close proximity, joined by polydentate ligands [3]. In this respect, the pyrazolato anion (and its ring-substituted derivatives) is an exobidentate ligand, showing the ability of bridging a variety of metal centers [4–6]. Single crystal X-ray diffraction studies on a number of binary 1,2-diazolates of copper(II) have revealed linear quasi-1D structures in which the metal ions are double bridged by pyrazolate ligands [7]. The magnetic properties of these pyrazolate systems are generally characterized by the presence of weak antiferromagnetic coupling between metal centers [8]. In contrast to the situation for 1,2-diazolates, structural studies on polymeric iron(II) 1,3-diazolate systems reveal only single imidazolate bridge [9]. One important consequence of the single azolate bridging in imidazolates has been the generation of extended structures with 3D

covalent connectivities. Another important characteristic property, not seen in corresponding pyrazolates, is that they exhibit antiferromagnetic coupling. T_C and long-range ferromagnetic ordering below that temperature. Such a behavior characterizes them as low-temperature molecular magnets [10]. $[\text{Fe}(\text{pz})_2]_x$ synthesis and magnetic susceptibility measurements were done by Patrick et al. [11] at an applied field of 10 kGauss over the temperature range 2–300 K. The plots of $\chi(T)$ and $\mu_{\text{eff}}(T)$ led to the observation of no maxima in the susceptibility plot on one hand and a decrease of μ_{eff} at low temperature on the other hand, which lets suggest a very weak antiferromagnetic coupling. A value of J equal to -0.59 cm^{-1} was obtained. A section of the extended structure of the complex is shown in Fig. 1. The two iron ions are linked by double pyrazolate bridges in the structure. The $\text{N}_{\text{pz}}-\text{Fe}-\text{N}_{\text{other pz}}$ angles are very close to the value for a regular tetrahedron. The empirical formula as given by Patrick et al. [11] is $\text{C}_6\text{H}_6\text{FeN}_4$ and the system crystallizes in orthorhombic symmetry with space group (SG) $Ibam$, #72.

In this work, we carry out an original and complementary study at the molecular and extended solid levels within DFT for $[\text{Fe}(\text{pz})_2]_x$. Exchange parameters J are obtained from molecular calculations in order to identify the ground state. The vibrational spectra (IR, Raman) are calculated providing a signature for the system. Non-magnetic calculations in the solid state allow addressing the instability of the system in such a configuration and assessing the chemical bonding. To stress the latter properties

* Corresponding author. Fax: +33 540002761.

E-mail address: s.matar@u-bordeaux1.fr (S.F. Matar).

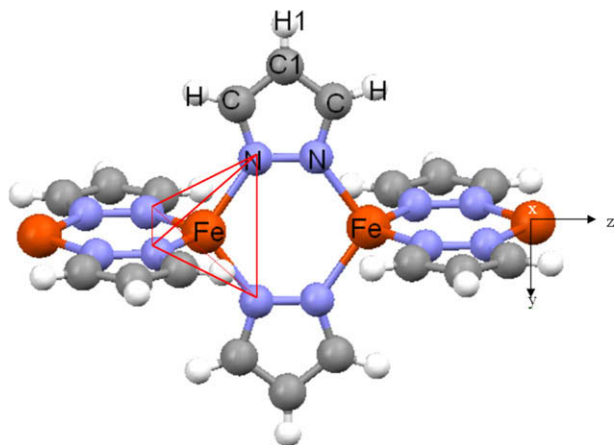


Fig. 1. Extended fragment view of $[\text{Fe}(\text{pz})_2]_x$. Fe atom is linked to four nitrogen belonging to two pyrazolate ligands and is shown within the tetrahedral environment of nitrogen. Coordinate axes show the orientation within the extended solid.

the electron localization map is provided. Then ferromagnetic (FM) and antiferromagnetic (AFM) configurations are considered in order to assess the ground state from energy differences. In another context, this double approach at the molecular and solid state levels allowed us addressing electronic structure properties of Fe^{II} spin cross-over systems [12] and Prussian-blue type complexes [13].

2. Computational details

2.1. Calculations for the molecular system

The use of Hartree–Fock (HF) approach provides a good description of the molecular orbital and chemical bonding properties of organic chemical systems. However it becomes well established that calling for the density functional theory (DFT) framework [14] brings far more accurate results regarding the energetics and related properties. This is because the compulsory exchange and correlation (XC) effects are equally treated, albeit at a local level, within DFT while only exchange is well accounted for in HF although in a better way (exact exchange [15]) than in DFT. Taking the best out of each one of the two approaches led to improvements in *ab initio* molecular calculations with the so called “hybrid functionals”. They consist of mixing exact HF exchange, e.g. following Becke [15] and DFT based correlation, e.g. following Lee, Yang and Parr, i.e., the so-called LYP correlation [16], with proportions that help to reproduce molecular properties of several systems. The calculations have been performed using Gaussian03 package [17]. In view of the difficulties found with Gaussian03 calculations for an accurate value of atomic spin densities, it was necessary to use the JAGUAR code [18] for defining the initial guess and to localize correctly the single electrons on different metal atoms especially in the case of BS (broken-symmetry) solution and then to generate an appropriate initial wave function set since it provides a better control of the local spin and multiplicities of the atoms. To maintain the electronic structure during the SCF procedure the quadratic convergence option was used. We have previously found that, among the most common functionals, the B3LYP hybrid one, combined with the broken-symmetry (BS) treatment [19,20], provides the best results for calculating coupling constants. In all calculations, the hybrid functional B3LYP and the LanL2DZ basis sets were used. The latter includes double- ζ with the Los Alamos effective core potential for Fe and the Dunning–Huzinaga all-electron double- ζ basis set with polarization functions for the H, C, and N

atoms (ζ is the exponent in the Gaussian type orbitals, GTO) [21,22]. The geometry was extracted from the CIF files (Crystallographic Information File). The following bond lengths used for the calculations were: $d_{\text{Fe-Fe}} = 3.880 \text{ \AA}$, $d_{\text{Fe-N}} = 2.027 \text{ \AA}$, $d_{\text{N-C}} = 1.337 \text{ \AA}$, $d_{\text{C-C}} = 1.370 \text{ \AA}$, $d_{\text{C-H}} = 0.964 \text{ \AA}$ [11].

2.2. Methodology for the extended solid approach

The all-electrons calculations are equally based on the DFT and the LDA as parametrized according to Vosko et al. [23]. They were performed with the augmented spherical wave (ASW) method [24,25] in which the wave function is expanded in atom-centered augmented spherical waves, which are Hankel functions and numerical solutions of Schrödinger’s equation, respectively, outside and inside the so-called augmentation spheres. In order to optimize the basis set, additional augmented spherical waves were placed at carefully selected interstitial sites (IS). The choice of these sites as well as the augmentation radii were automatically determined using the sphere-geometry optimization algorithm [26]. Self-consistency was achieved by a highly efficient algorithm for convergence acceleration [27]. The use of this method in molecular based systems was formerly validated by Eyert et al. [28]. The Brillouin zone integrations were performed using the linear tetrahedron method with up to 279 k -points within the irreducible wedge [24,25,29]. In the minimal ASW basis set [25] we chose the outermost shells to represent the valence states and the matrix elements were constructed using partial waves up to $l_{\text{max}} + 1 = 3$ for Fe and $l_{\text{max}} + 1 = 2$ for C, N and H, where l is the secondary quantum number. The completeness of the valence basis set was checked for charge convergence meaning that charge residues are ≤ 0.1 for $l_{\text{max}} + 1$. The self-consistent field calculations were run to a convergence of $\Delta Q = 10^{-8}$ for the charge density [27] and the accuracy of the method is in the range of about 10^{-8} eV regarding energy differences. In the context of this study, ASW–LDA was used in order to obtain a description of the electronic structure with the site projected density of states PDOS.

The chemical bonding is assessed by using the crystal orbital overlap population (COOP) criterion [30] based on the expectation values of operators which consist of the non-diagonal elements of the overlap population matrix. Positive and negative contributions indicate bonding and antibonding states, respectively. In this work we use integrated partial COOP (iCOOP) for a comparison of the relative strengths of the atom-to-atom chemical bonding.

Further an insight into the localization of electrons around the chemical constituents is provided from the calculations, based on the electron localization function (ELF) [31]. It allows determining the amount of localization of electrons with respect to the free electron gas distribution. The dimensionless ELF magnitude ranges from 0 to 1 with $\text{ELF} = 1/2$ corresponding to the free electron gas distribution. These three extreme situations will be illustrated by three sets of colors: $\text{ELF} = 0$ points to no localization (blue contours), $\text{ELF} = 1$ points to strong localization (red contours) and $\text{ELF} = 1/2$ with green contours (cf. Fig. 5).

Three types of computations for the complex system were carried out assuming firstly a non-magnetic configuration. Such a first approach allows to get an insight into the quantum mixing of the valence states leading to the analysis of the chemical bonding as well to detect an instability of the NM configuration versus spin polarization. In as far as these calculations assume spin degeneracy for all species, they are labeled as non-spin polarized (NSP). Spin polarized (SP) magnetic calculations are done subsequently with an implicit ferromagnetic order (FM). Such a configuration is then confronted with antiferromagnetic (AFM) one in order to establish the ground state expected for $[\text{Fe}(\text{pz})_2]_x$ from energy differences.

Download English Version:

<https://daneshyari.com/en/article/5375593>

Download Persian Version:

<https://daneshyari.com/article/5375593>

[Daneshyari.com](https://daneshyari.com)