

On the Relevance of an Antiferromagnetic Dimer Model for the Spin-Gapped Magnetic Solids Cu(terpy)Mo₂O₇ and Cu(OH)(*p*-pyc)H₂O

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The magnetic solids Cu(terpy)Mo₂O₇ (terpy = terpyridine) and Cu(OH)(*p*-pyc)H₂O (*p*-pyc = *p*-pyridinecarboxylate) have a spin gap and possess chains of Cu²⁺ ions in which two different Cu···Cu distances alternate. On the basis of their reported crystal structures, the spin-exchange interactions of these compounds were examined by performing spin dimer analysis to determine whether an antiferromagnetic dimer or an alternating antiferromagnetic chain model is appropriate for their magnetic properties. Our analysis shows that an antiferromagnetic dimer model is correct for both compounds because of the anisotropic overlap between the magnetic orbitals of their Cu²⁺ sites.

1. Introduction

Magnetic properties of a solid with unpaired spins are commonly described by a Heisenberg spin Hamiltonian written as a sum of pairwise isotropic spin-exchange interactions. The spin–lattice of a magnetic solid is determined by the repeat pattern of its strongly interacting spin-exchange interactions. For instance, a magnetic solid described by an alternating antiferromagnetic (AFM) chain model has chains of alternating exchange interactions *J* and *J'*. Given a spin–lattice, the energy differences between its different magnetic states are expressed in terms of the spin-exchange parameters. In the analysis of the magnetic susceptibility data with a spin Hamiltonian, the associated exchange parameters become numerical fitting parameters that reproduce the experimental data.¹ This fitting analysis may not provide a unique solution, and there are cases when magnetic susceptibility data can be fitted equally well with more than one spin–lattice model. For example, vanadyl pyrophosphate (VO)₂P₂O₇ has a spin gap and its magnetic susceptibility can be described by

alternating AFM chain² and two-leg spin ladder³ models. It is an important issue to determine which model is correct in such a case. An alternating AFM chain model was proven to be correct for (VO)₂P₂O₇ by neutron scattering experiments⁴ with oriented crystal samples and also by spin dimer analysis based on tight-binding electronic structure calculations.^{1,5}

Among numerous metal–organic framework compounds,⁶ two compounds alternate chains of Cu²⁺ ions, namely, Cu(terpy)Mo₂O₇ (terpy = terpyridine)⁷ and Cu(OH)(*p*-pyc)H₂O (*p*-pyc = *p*-pyridinecarboxylate).⁸ Both compounds have a

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spin gap and are almost equally well described by AFM dimer and alternating AFM chain models.^{7,8} An alternating AFM chain model becomes an isolated AFM dimer model when the ratio $\alpha = J'/J$ is reduced to zero. It is often difficult to distinguish an isolated AFM dimer model from an alternating AFM chain model with small $\alpha = J'/J$. In the fitting analysis of susceptibility data, there are a number of parameters to fit other than J' and J (e.g., the g factor, the temperature-independent susceptibility, the mole fraction of paramagnetic impurities, and the Curie–Weiss temperature). In such a case, spin dimer analysis can provide a decisive answer as to which model is correct.¹ In the present work, we examine the spin-exchange interactions of the two spin-gapped systems $\text{Cu}(\text{terpy})\text{Mo}_2\text{O}_7$ and $\text{Cu}(\text{OH})(p\text{-pyc})\text{H}_2\text{O}$ by performing spin dimer analysis¹ on the basis of their reported crystal structures^{7,8} to show that a key to deciding which model is correct is to consider the anisotropic overlap between the magnetic orbitals of their Cu^{2+} sites.

2. Spin Dimer Analysis

The spin-exchange parameters of a magnetic solid are estimated on the basis of first principles electronic structure theory either by calculating the electronic structures for the high- and low-spin states of various spin dimers (i.e., structural units consisting of two spin sites) of the solid⁹ or by calculating the electronic band structures for various ordered spin states of the solid.¹⁰ The energy differences between different electronic states are then mapped onto the corresponding energy differences given by the spin Hamiltonian employed.^{1,11} In an explanation of the trends in spin-exchange interactions of magnetic solids or testing of the validity of a spin–lattice model chosen to construct a spin Hamiltonian, it is often sufficient to evaluate the relative strengths of the spin-exchange interactions by performing spin dimer analysis based on extended Hückel tight-binding (EHTB) calculations.¹² In this approach, a spin-exchange parameter J is written as $J = J_F + J_{\text{AF}}$,¹³ and AFM spin-exchange interactions (i.e., $J < 0$) are discussed by focusing on the AFM terms J_{AF} because the ferromagnetic term J_F (> 0) is a small positive number. The AFM spin-exchange term J_{AF} between spin $1/2$ sites is given by¹

$$J_{\text{AF}} \approx -(\Delta e)^2/U_{\text{eff}} \quad (1)$$

where Δe is the energy split when the two magnetic orbitals of a spin dimer interact. Because the effective on-site

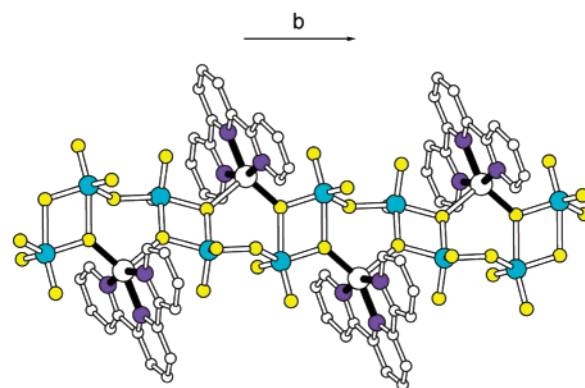


Figure 1. Perspective view of one $\text{Cu}(\text{terpy})\text{Mo}_2\text{O}_7$ chain. The large white, cyan, blue, yellow, and small white circles represent Cu, Mo, N, O, and C atoms, respectively. For simplicity, the H atoms are not shown.

repulsion U_{eff} is approximately constant for a given magnetic ion in a closely related series of compounds, the trends in the J_{AF} values are estimated by those in the corresponding $(\Delta e)^2$ values. In the present work, the $(\Delta e)^2$ values for the spin dimers of $\text{Cu}(\text{terpy})\text{Mo}_2\text{O}_7$ and $\text{Cu}(\text{OH})(p\text{-pyc})\text{H}_2\text{O}$ were calculated by performing EHTB electronic structure calculations with the atomic parameters listed in the Table S1 of the Supporting Information.^{14–16}

3. Results and Discussion

A. $\text{Cu}(\text{terpy})\text{Mo}_2\text{O}_7$. As depicted in Figure 1, $\text{Cu}(\text{terpy})\text{Mo}_2\text{O}_7$ consists of Mo_2O_7 chains made up of edge- and corner-sharing MoO_5 square pyramids.⁷ Each Mo_2O_7 chain becomes a $\text{Cu}(\text{terpy})\text{Mo}_2\text{O}_7$ chain by incorporating Cu^{2+} ions and terpy molecules such that each Cu^{2+} ion forms a distorted CuN_3O_2 square pyramid with every terpy molecule arranged approximately perpendicular to the Mo_2O_7 chain. The basal plane of each CuN_3O_2 square pyramid consists of three N atoms and one O atom, as depicted in Figure 2a, where the Cu–O and Cu–N bonds approximately parallel to the basal plane are highlighted in black. It should be noted that the magnetic orbital of a spin monomer, $[\text{Cu}(\text{terpy})\text{O}_2]^{2-}$, is contained in the basal plane of its CuN_3O_2 square pyramid (Figure 2b). For the convenience of our discussion, we denote the basal and apical O atoms of a CuN_3O_2 square pyramid as the O_{bs} and O_{ap} atoms, respectively. In a $\text{Cu}(\text{terpy})\text{Mo}_2\text{O}_7$ chain, there are two types of spin-exchange interactions. The super-superexchange interaction J (Figure 3a) has the Cu– $\text{O}_{\text{bs}}\cdots\text{O}_{\text{bs}}$ –Cu contact across the Mo_2O_2 rhombus with $\text{Cu}\cdots\text{Cu} = 6.251 \text{ \AA}$, and the super-superexchange interaction J' (Figure 3b) has the Cu– $\text{O}_{\text{ap}}\cdots\text{O}_{\text{ap}}$ –Cu contact across the Mo_2O_2 rhombus with $\text{Cu}\cdots\text{Cu} = 6.816 \text{ \AA}$. Zubieta and co-workers found⁷ that the magnetic susceptibility data of $\text{Cu}(\text{terpy})\text{Mo}_2\text{O}_7$ are almost equally well fitted by alternating AFM chain and AFM dimer models. Namely, an AFM dimer model gave $g = 2.13$, $J/k_B = -27.1 \text{ K}$, $\chi_{\text{TI}} = -0.00003 \text{ cm}^3/\text{mol}$, and $x = 0.001$, while an alternating

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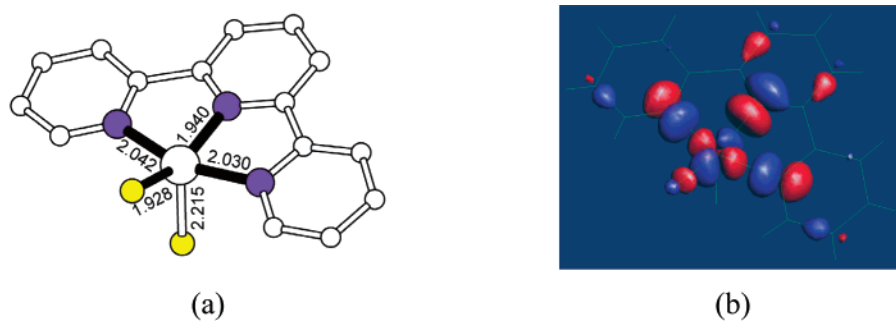


Figure 2. (a) Perspective view and (b) magnetic orbital of a distorted square pyramid CuN_3O_2 in $\text{Cu}(\text{terpy})\text{Mo}_2\text{O}_7$. The Cu–O and Cu–N bonds approximately parallel to the basal plane of the CuN_3O_2 square pyramid are highlighted in black.

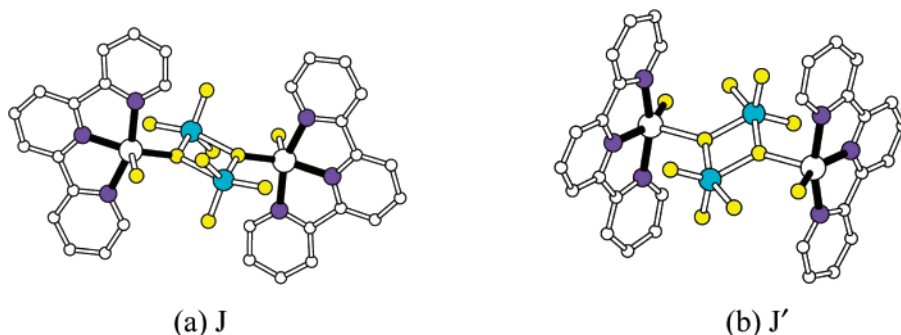


Figure 3. Spin dimers of $\text{Cu}(\text{terpy})\text{Mo}_2\text{O}_7$ associated with the exchange paths (a) J and (b) J' . The Cu–O and Cu–N bonds approximately parallel to the basal plane of each CuN_3O_2 square pyramid are highlighted in black.

AFM chain model gave $g = 2.17$, $J/k_B = -26.5$ K, $\alpha = J'/J = 0.170$, $\chi_{\text{TI}} = -0.000\ 03$ cm^3/mol , and $x = 0.0010$. From these fitting results alone, it is difficult to decide which model is correct.

Given that in each $\text{Cu}(\text{terpy})\text{Mo}_2\text{O}_7$ chain the $\text{Cu}\cdots\text{Cu}$ distances of 6.251 and 6.816 Å alternate, one might prefer the alternating AFM chain model. However, this model is not consistent with the electronic structure of $\text{Cu}(\text{terpy})\text{Mo}_2\text{O}_7$. As depicted in Figure 2b, the magnetic orbital of each Cu^{2+} site is contained in the basal plane of the CuN_3O_2 square pyramid and has a nonzero orbital contribution on the O_{bs} atom but has no orbital contribution on the O_{ap} atom. As a consequence, the magnetic orbitals have a nonzero overlap through the $\text{Cu}-\text{O}_{\text{bs}}\cdots\text{O}_{\text{bs}}-\text{Cu}$ path but have no overlap through the $\text{Cu}-\text{O}_{\text{ap}}\cdots\text{O}_{\text{ap}}-\text{Cu}$ path. Consequently, the spin exchange J' should be negligible, and only the spin exchange J should be responsible for the magnetic susceptibility of $\text{Cu}(\text{terpy})\text{Mo}_2\text{O}_7$. Thus, an AFM dimer model is expected to be correct for $\text{Cu}(\text{terpy})\text{Mo}_2\text{O}_7$. This is confirmed by our calculations of the $(\Delta e)^2$ values (Table 1).

B. $\text{Cu}(\text{OH})(p\text{-pyc})\text{H}_2\text{O}$. In $\text{Cu}(\text{OH})(p\text{-pyc})\text{H}_2\text{O}$,⁸ each Cu^{2+} ion forms a CuNO_4 square pyramid with two $p\text{-pyc}$ and three hydroxide (HO^-) anions, as shown in Figure 4a, where the H atoms of the three HO^- ions are not shown for simplicity. The four basal corners of the CuNO_4 square pyramid consist of the N atom of one $p\text{-pyc}$ anion, one O atom of another $p\text{-pyc}$ anion, and two HO^- anion O atoms. As shown in Figure 5a, a two-dimensional (2D) layer of composition $\text{Cu}(\text{OH})(p\text{-pyc})$ is obtained by edge-sharing the basal HO^- anions of the CuNO_4 square pyramids. These 2D layers are stacked such that each basal HO^- ion of one Cu^{2+} ion occupies the apical position of its adjacent Cu^{2+} ion

Table 1. Geometrical Parameters and $(\Delta e)^2$ Values Associated with the Spin-Exchange Paths of $\text{Cu}(\text{terpy})\text{Mo}_2\text{O}_7$ and $\text{Cu}(\text{OH})(p\text{-pyc})\text{H}_2\text{O}^a$

path	Cu \cdots Cu	O \cdots O	$(\Delta e)^2$
(a) $\text{Cu}(\text{terpy})\text{Mo}_2\text{O}_7$			
J	6.251	2.423	970 (1.00)
J'	6.816	2.407	10 (0.01)
(b) $\text{Cu}(\text{OH})(p\text{-pyc})\text{H}_2\text{O}$			
J	2.965		6360 (1.00)
J'	3.107		370 (0.06)
J''	8.803		3580 (0.56)

^a The distances are in units of angstroms and the $(\Delta e)^2$ values in units of millelectronvolts squared. The numbers in parentheses are the relative numbers with respect to the strongest interaction.

(Figure 5b). In the resulting three-dimensional (3D) network of $\text{Cu}(\text{OH})(p\text{-pyc})\text{H}_2\text{O}$, there occur chains of alternating Cu_2O_2 rhombi with $\text{Cu}\cdots\text{Cu}$ distances of 2.965 and 3.107 Å, respectively. Given that $\text{Cu}(\text{OH})(p\text{-pyc})\text{H}_2\text{O}$ has chains of alternating $\text{Cu}\cdots\text{Cu}$ distances (i.e., 2.965 and 3.107 Å), one might consider describing the magnetic susceptibility of $\text{Cu}(\text{OH})(p\text{-pyc})\text{H}_2\text{O}$ in terms of an alternating AFM chain or an AFM dimer model. Oliver and co-workers showed⁸ that an AFM dimer model is correct for $\text{Cu}(\text{OH})(p\text{-pyc})\text{H}_2\text{O}$, and their fitting analysis led to $g = 2.18$ and $J/k_B = -141$ K.

In $\text{Cu}(\text{OH})(p\text{-pyc})\text{H}_2\text{O}$, there are three different types of spin-exchange interactions, J (Figure 6a), J' (Figure 6b), and J'' (Figure 6c), to consider. It is desirable to find which of these interactions is responsible for the AFM dimer behavior of $\text{Cu}(\text{OH})(p\text{-pyc})\text{H}_2\text{O}$. As depicted in Figure 4b, the magnetic orbital of each Cu^{2+} site is contained in the basal plane of the CuNO_4 square pyramid. In the exchange interaction J' , the magnetic orbitals are parallel and are separated by the distance of approximately the $\text{Cu}-\text{O}_{\text{ap}}$ bond

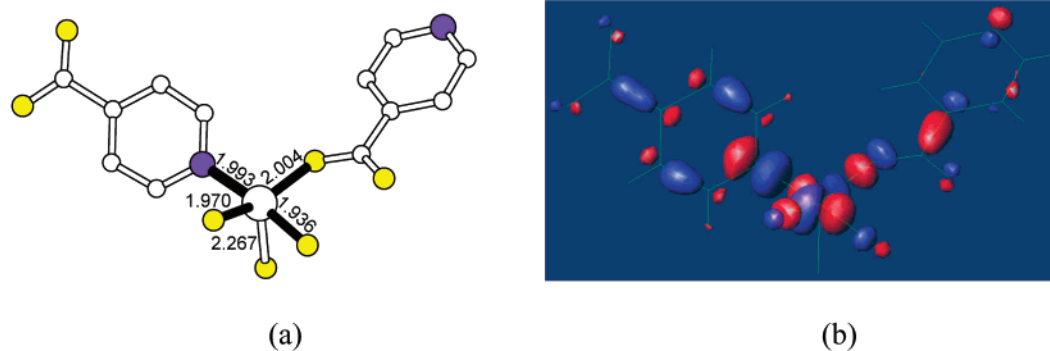


Figure 4. (a) Perspective view and (b) magnetic orbital of a distorted square pyramidal CuNO_4 in $\text{Cu}(\text{OH})(p\text{-pyc})\text{H}_2\text{O}$. The large white, blue, yellow, and small white circles represent Cu, N, O, and C atoms, respectively. The Cu–O and Cu–N bonds approximately parallel to the basal plane of the CuNO_4 square pyramid are highlighted in black. For simplicity, the H atoms are not shown.

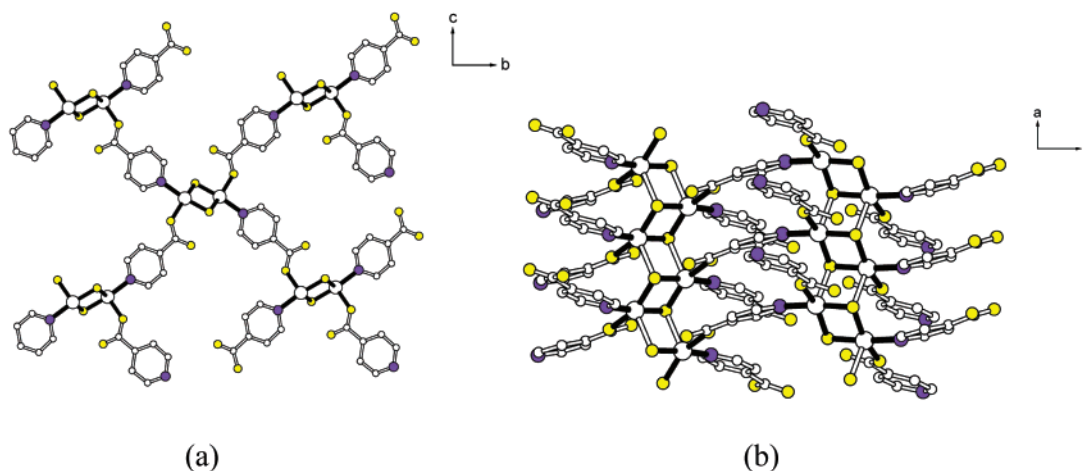


Figure 5. (a) Projection view of a layer of composition $\text{Cu}(\text{OH})(p\text{-pyc})$ in $\text{Cu}(\text{OH})(p\text{-pyc})\text{H}_2\text{O}$. (b) Projection view of $\text{Cu}(\text{OH})(p\text{-pyc})\text{H}_2\text{O}$ obtained by stacking the $\text{Cu}(\text{OH})(p\text{-pyc})$ layers. For simplicity, the H_2O molecules are not shown. The Cu–O and Cu–N bonds approximately parallel to the basal plane of each CuNO_4 square pyramid are highlighted in black.

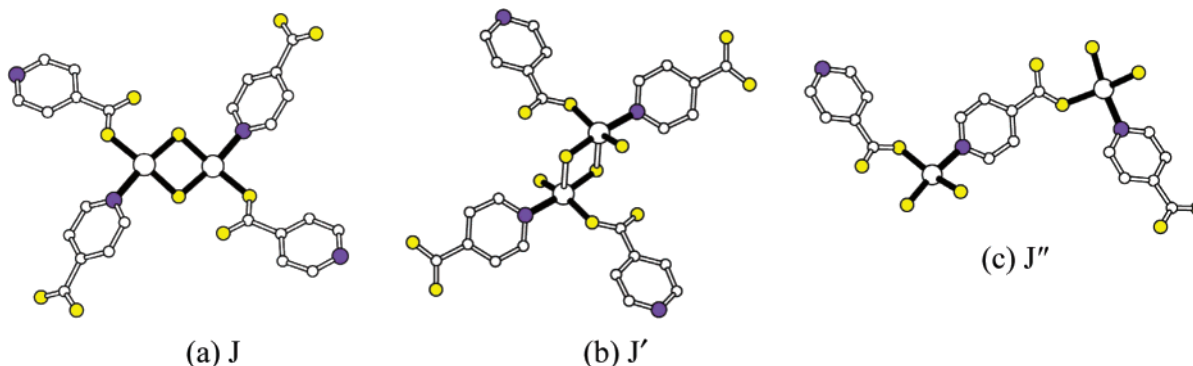


Figure 6. Spin dimers of $\text{Cu}(\text{OH})(p\text{-pyc})\text{H}_2\text{O}$ associated with the exchange paths (a) J , (b) J' , and (c) J'' . The Cu–O and Cu–N bonds approximately parallel to the basal plane of each CuNO_4 square pyramid are highlighted in black.

length, and hence their overlap is negligible. This makes the exchange interaction J' negligible compared with J , as can be seen from the calculated $(\Delta e)^2$ values (Table 1). Thus, each chain of alternating Cu_2O_2 rhombi consists of isolated AFM dimers, as far as the spin-exchange interactions J and J' are concerned.

The chains of alternating Cu_2O_2 rhombi are interconnected through the $p\text{-pyc}$ anions (Figure 5a). Our $(\Delta e)^2$ calculations suggest that the exchange J'' is quite substantial compared with the exchange J (i.e., $J''/J \approx 0.56$). Such J and J'' parameters lead to a 2D spin–lattice, which is in contradiction to the fact that the magnetic susceptibility of $\text{Cu}(\text{OH})$ -

$(p\text{-pyc})\text{H}_2\text{O}$ is described by an AFM dimer model. In our EHTB calculations, the exchange J'' is strong because each $p\text{-pyc}$ anion acts as an efficient unit for coupling adjacent Cu^{2+} ions, which originates from the fact that the N and O p_σ orbitals contribute almost equally in the two molecular orbitals of a $p\text{-pyc}$ anion representing the N and O lone pairs (Figure 7a,b). This finding would be an artifact of EHTB calculations, which do not adjust the potentials self-consistently and consequently do not distinguish the potential difference between the anion and neutral ends of a $p\text{-pyc}$ anion. To verify this point, we carried out density functional theory (DFT) electronic structure calculations for a $p\text{-pyc}$

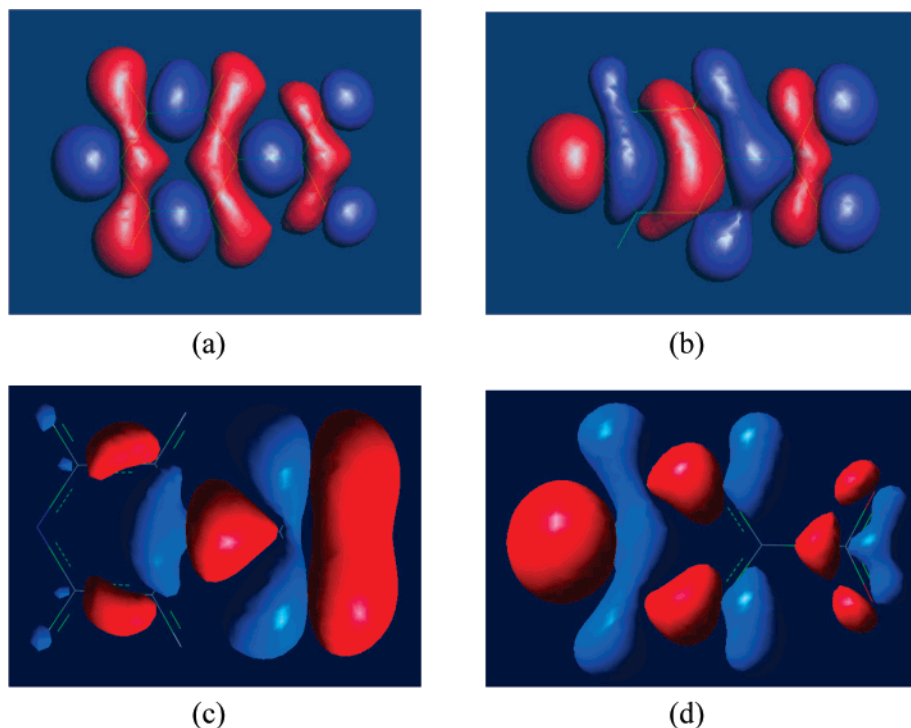


Figure 7. 3D surface plots of the two molecular orbitals of a *p*-pyc anion that represent the N and O lone pairs. The N and O p_{σ} orbitals have almost equal contributions to the molecular orbitals determined from EHTB calculations in parts a and b but strongly unequal contributions to the molecular orbitals determined from DFT calculations in parts c and d.

anion with the 6-31G* basis set and the B3LYP functional¹⁷ using the *Gaussian 03* program package.¹⁸ As expected, the DFT calculations show strongly unequal N and O p_{σ} orbital contributions in the two molecular orbitals representing the N and O lone pair orbitals (Figure 7c,d). Thus, a *p*-pyc anion should not act as an effective spin-coupling unit between two Cu^{2+} sites, and the exchange J' should be negligible. In short, the magnetic susceptibility of $\text{Cu}(\text{OH})(p\text{-pyc})\text{H}_2\text{O}$ should be primarily determined by the spin exchange J and therefore should be described by an AFM dimer model.

C. Comparison between $\text{Cu}(\text{terpy})\text{Mo}_2\text{O}_7$ and $\text{Cu}(\text{OH})(p\text{-pyc})\text{H}_2\text{O}$. The fitting analyses of the magnetic susceptibilities of $\text{Cu}(\text{terpy})\text{Mo}_2\text{O}_7$ and $\text{Cu}(\text{OH})(p\text{-pyc})\text{H}_2\text{O}$ using an AFM dimer model show that the spin exchange is stronger for $\text{Cu}(\text{OH})(p\text{-pyc})\text{H}_2\text{O}$ than for $\text{Cu}(\text{terpy})\text{Mo}_2\text{O}_7$ by a factor of 5.2 (i.e., $J/k_{\text{B}} = -141$ vs -27.1 K).^{4,7} According to the corresponding $(\Delta e)^2$ values, the spin exchange is stronger for $\text{Cu}(\text{OH})(p\text{-pyc})\text{H}_2\text{O}$ than for $\text{Cu}(\text{terpy})\text{Mo}_2\text{O}_7$ by a factor of 6.6 [i.e., $(\Delta e)^2 = 6360$ vs 970 meV²]. This agreement between theory and experiment is quite reasonable in view of the approximate nature of the spin dimer analysis employed.

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4. Concluding Remarks

The structures of both $\text{Cu}(\text{terpy})\text{Mo}_2\text{O}_7$ and $\text{Cu}(\text{OH})(p\text{-pyc})\text{H}_2\text{O}$ exhibit chains of Cu^{2+} ions in which two different $\text{Cu}\cdots\text{Cu}$ distances alternate. Thus, one might consider describing their magnetic susceptibilities using an alternating AFM chain model with two exchange interactions J and J' . However, one of the interactions becomes negligible because of the anisotropic shape of the magnetic orbital at each Cu^{2+} site and the way the planes of the magnetic orbitals are arranged. Therefore, the magnetic susceptibilities of both $\text{Cu}(\text{terpy})\text{Mo}_2\text{O}_7$ and $\text{Cu}(\text{OH})(p\text{-pyc})\text{H}_2\text{O}$ should be described by an AFM dimer model. Our analysis points out the importance of considering the anisotropic overlap between magnetic orbitals in selecting a spin–lattice model.

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Supporting Information Available: Table S1 of the atomic parameters employed for the EHTB calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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