Influence of Jahn-Teller Distortion on the Magnetic Coupling in Oxalato-Bridged Copper(II) Dimers: An Orbital Interpretation of the Superexchange Mechanism

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Extended Hückel molecular calculations have been used to analyze how the magnitude of exchange coupling is influenced by the structural distortions in a series of dinuclear six-coordinate copper(II) complexes bridged by the planar bis-bidentate oxalate anion. Copper(II) ions have distorted octahedral surroundings, one being axially elongated and the other compressed. The magnetic interaction is strong in the former complexes and very weak in the latter. This is interpreted as resulting from a switching of magnetic spin orbitals due to the structural distortions (bond elongation or compression) of the copper sites.

Key Words : Spin dimer, Superexchange, Magnetic coupling, Extended Hückel

Introduction

Magnetic properties of dinuclear μ-oxalato copper(II) complexes have been of interest for some time. In part, this is because of the ability of a bridging ligand to provide a pathway for exchange coupling between transition metal ions separated by more than 5 Å. The magnetic interactions of dinuclear oxalato bridged complexes have been thoroughly discussed by Hoffmann[1] and Kahn.[2] The theories presented by these authors have been used to rationalize the magnetic interactions observed for the oxalato-bridged copper(II) compounds.[3]

Recent theoretical and experimental works[4] have revealed that the exchange interactions between the copper ions propagated through the oxalate bridge are strongly dependent on the coordination environment around the copper ions. When the short copper-ligand bonds are coplanar with the bridging ligand, the strong antiferromagnetic coupling results. In such case, the spin orbitals of copper(II) ions are well oriented to interact with the oxalate orbitals. Otherwise, the interaction between the spin orbitals through the bridge becomes poor and weak coupling results.

The μ-oxalato-dicopper(II) complexes have rich stereochemistry because of the plasticity of the coordination sphere of this metal ion which can be four-, five- or six-coordinated.[5] The octahedral compounds of varying structural complexity through pronounced Jahn-Teller distortion are also known.[6-12] Although the Jahn-Teller effect is well documented in the chemistry of copper(II), its influence on the magnitude of the exchange coupling in polynuclear copper(II) complexes remained unexplored most likely because of the lack of copper(II) dimers exhibiting a compressed octahedral environment. It is noteworthy in this regard that the μ-oxalato-dicopper(II) complexes whose structures have been recently reported[12] have exhibited an axially-compressed (2+4) geometry rather than the more common axially-elongated (4+2) structure. Concerning the coordination geometry, two situations are possible. If the ligands along the z-axis are further away from the copper(II)

center than those in the *xy* plane, then we expect the x^2-y^2 (or *xy*) orbital to be singly occupied and highest in energy. For the case where the geometry is axially compressed along *z* the converse will occur and now the z^2 orbital will be higher and singly occupied. In this paper, we will consider this point to present the results of extended Hückel molecular orbital (EHMO) calculations[13,14] on model dimers of general formula $[(H_3N)_4Cu(\mu\text{-}C_2O_4)Cu(NH_3)_4]^{2+}$ in an attempt to obtain semiquantitative estimates of the effect of the distortions of the local copper octahedral geometry on the magnetic coupling. The atomic parameters used in our calculations are collected in Table 1.

Description of Model Complexes

The geometrical features and exchange coupling constants for a variety of oxalato-bridged copper compounds are presented in Table 2. The coordination geometry of copper(II) is divided into two classes in these compounds. In each axially-compressed (2+4) octahedral complex, the axial bonds are shorter than the equatorial distances. In order to investigate a significant influence of this structural feature on the magnetic coupling interaction, we modeled the

Table 1. Exponents ζ_i and valence shell ionization potentials H_{ii} of Slater-type orbitals χ_i used for extended Hückel MO calculations

atom	χ_i	H_{ii}(eV)	ζ_i	C_i	ζ_i'	C_i'
Cu	4s	−11.4	2.151	1.0		
Cu	4p	−6.06	1.370	1.0		
Cu	3d	−14.0	7.025	0.4473	3.004	0.6978
O	2s	−32.3	2.688	0.7076	1.675	0.3745
O	2p	−14.8	3.694	0.3322	1.659	0.7448
N	2s	−26.0	2.261	0.7297	1.425	0.3455
N	2p	−13.4	3.249	0.2881	1.499	0.7783
C	2s	−21.4	1.831	0.7931	1.153	0.2739
C	2p	−11.4	2.730	0.2595	1.257	0.8026
H	1s	−13.6	1.300	1.0		

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Table 2. Structural and magnetic data for selected oxalato-bridged Cu(II) complexes

compound[a]	chromophore	geometry	J (cm^{-1})	ref.
[Cu$_2$(dpyam)$_4$(C$_2$O$_4$)](ClO$_4$)$_2$(H$_2$O)$_3$	N$_2$O$_2$N'$_2$	2+4	2.42	12
[Cu$_2$(dpyam)$_4$(C$_2$O$_4$)](BF$_4$)$_2$(H$_2$O)$_3$	N$_2$O$_2$N'$_2$	2+4	3.38	12
[Cu$_2$(dpyam)$_2$(C$_2$O$_4$)(NO$_3$)$_2$((CH$_3$)$_2$SO)$_2$]	N$_2$O$_2$O'O"	4+2	−305	12
[Cu$_2$(bpy)$_2$(C$_2$O$_4$)(NO$_3$)$_2$(H$_2$O)$_2$]	N$_2$O$_2$O'O"	4+2	−382	6
[Cu$_2$(deen)$_2$(C$_2$O$_4$)(ClO$_4$)$_2$(H$_2$O)$_2$]	N$_2$O$_2$O'O"	4+2	−300	8
[Cu$_2$(tacn)$_2$(C$_2$O$_4$)(ClO$_4$)$_2$]	N$_3$O$_2$O'	2+4	−41	9
[Cu$_2$(bispicen)$_2$(C$_2$O$_4$)](ClO$_4$)$_2$	N$_2$O$_2$N'$_2$	2+4	−2.3	11
[Cu$_2$(bispicMe$_2$en)$_2$(C$_2$O$_4$)](ClO$_4$)$_2$	N$_2$O$_2$N'$_2$	2+4	−2.14	11

[a]dpyam = di-2-pyridylamine; bpy = 2,2'-dipyridine; deen = N,N-diethylethane-1,2-iamine; tacn = 1,4,7-triazacyclononane; bispicen = N,N'-bis(2-pyridylmethyl)-1,2-ethanediamine; bispicMe$_2$en = N,N'-bis(2-pyridylmethyl)-N,N-dimethyl-1,2-ethanediamine
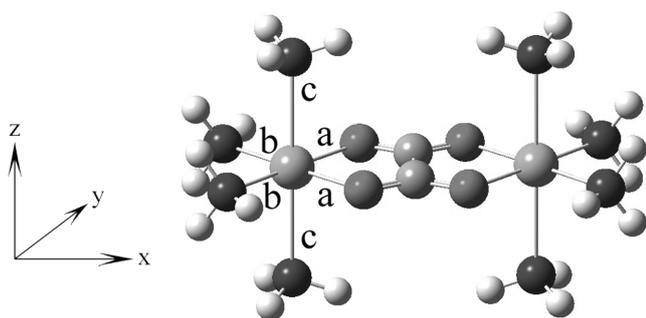
Figure 1. Perspective views of [Cu$_2$(C$_2$O$_4$)(NH$_3$)$_8$]$^{2+}$ dinuclear model with [Cu(C$_2$O$_4$)(NH$_3$)$_4$] monomeric unit used in theoretical calculations. The two copper(II) spin centers are coplanar with the oxalate bridge.

Figure 2. Plot of the energy of *xy* and *z^2* spin orbitals from EH calculations for the hypothetical [Cu(C$_2$O$_4$)(NH$_3$)$_4$] mononuclear complex as a function of the metal to ligand bond distances (see text).

geometry as placing the copper atoms in a distorted octahedral environment. All the non-bridging ligands were replaced by ammonia molecules. The equatorial planes of copper coordination spheres were kept in a plane. All the bond lengths in the models were obtained by averaging the corresponding experimental data. The bond angles are close to those reported for the experimental complexes. The model complex [(NH$_3$)$_4$Cu(C$_2$O$_4$)Cu(NH$_3$)$_4$]$^{2+}$ is shown in Figure 1 together with the relevant geometrical parameters of [(NH$_3$)$_4$Cu(C$_2$O$_4$)] monomeric unit which are used in the calculations. Calculations for the model compounds were performed for these different bond distances around the copper atom with the following structural parameters: N-H = 1.02 Å; C-C = 1.56 Å; C-O = 1.25 Å; C-C-O = 117°; Cu-N-H = 109°; O-Cu-N$_{eq}$ = 93°.

Results and Discussion

When no direct metal-metal bond occurs, the exchange interaction between adjacent spin centers in complexes is due to the delocalization of the spin density onto orbitals of the bridging ligands that connect the centers.[1,15] For a system with two metal atoms each bearing one unpaired electron, the magnetic coupling constant J is given, according to Hoffmann's expression,[1] by Equation (1).

$$E(singlet) - E(triplet) = J = 2K_{ab} - (\Delta e)^2/(J_{aa} - J_{ab}) \qquad (1)$$

Here, K$_{ab}$, J$_{aa}$ and J$_{ab}$ are the exchange integral, the one- and

two-center Coulomb repulsion integrals, respectively, and Δe is the difference in energy between the two singly occupied molecular orbitals (SOMOs) of a spin dimer formed from the two spin orbitals originally describing the unpaired electrons. Of the two terms on the right of eqn. (1), the first one can be interpreted as a ferromagnetic contribution J$_F$ to the magnetic exchange constant, favoring the triplet ground state (*i.e.*, J > 0), while the second one represents an antiferromagnetic contribution J$_{AF}$ favoring the singlet ground state (*i.e.*, J < 0). The nature of the interaction will be ferro- or antiferromagnetic depending upon whether parallel or antiparallel spin coupling, respectively, is found in the ground state. If it is assumed that all two-electron integrals are very small and invariant for the slight changes in structural parameters within a family of compounds with the same magnetic centers and bridging ligand, the variations in J parameters of a magnetic system can be expected to arise from the corresponding Δe values. When Δe is large, the corresponding J is dominated by the J$_{AF}$ term which is always negative. When Δe is zero or nearly zero, the positive J$_F$ term is predominant. The interaction of the metal and ligand orbitals thus affects the energy splitting of the two SOMOs and determines whether the spin exchange mech-

anism results in overall antiferromagnetism or ferromagnetism. The main focus in this paper is placed on electronic structure analysis of the dependence of the magnetic coupling constants on the specific changes in structures, rather than calculations of the coupling constant. In the μ-oxalato-bridged dicopper(II) complexes, the antiferromagnetic coupling interaction between the two magnetic centers occurs through superexchange via the μ-oxalato bridging ligand, where the overlap between the singly occupied metal d orbital on the metal atoms and the oxygen p orbitals on the bridging ligand is responsible for the magnetic superexchange coupling. The extent of the coupling depends on the magnitude of the overlap between the spin orbitals of the two magnetic centers and the lower-lying filled orbitals of the bridging ligand. The more negative overlap indicates a stronger antibonding interaction between the metal and the ligand orbitals which results in a larger energy gap between SOMOs and in a greater superexchange coupling.

The remarkable variation of J values for the family of compounds reported in Table 2 is strongly dependent on the coordination geometry around the Cu(II) ions. The large coupling in the (4+2) axially-elongated system arises from the strong σ overlap between the copper d_{xy} (xy) spin orbitals through the oxalate O atoms. On the contrary, in the (2+4) axially-compressed system, the copper centers have a d_{z^2} (z^2) spin orbital which overlaps very poorly with the oxalate σ orbitals and leads to a considerably weaker coupling as observed. A superexchange pathway involving the π system is unlikely because of symmetry mismatch of the relevant ligand orbitals and the copper spin orbitals in the octahedral geometries. Thus the mechanism of exchange interaction between the two magnetic centers occurs through the s system of the bridging ligand.

Before discussing the electronic structure of the d^9 model complex $[(H_3N)_4Cu(\mu\text{-}C_2O_4)Cu(NH_3)_4]^{2+}$, it is convenient to define a local coordinate system for each Cu ion. Accordingly, the z axis at each Cu center is chosen such that it is parallel to the appropriate Cu-N_{ax} bond axis, and the x axis is defined so that the Cu-Cu vector lies in the xz plane, as shown in Figure 1. Using this definition, the octahedral t_{2g} orbitals on each Cu center correspond to x^2-y^2, xz, yz, and the higher-lying e_g orbitals to z^2 and xy. Low-symmetry distortions, such as the nonequivalence of N and O donors, the different copper-donor bond lengths and bond angles, remove the degeneracy of the parent t_{2g} and e_g orbitals.

One can now try to get a deeper understanding of the exchange interaction operating in the compounds described in the present study. In the case of Cu(II) ions, the unpaired electron, which occupies an xy orbital in a (4+2) environment, is located in the z^2 orbital in a (2+4) one. Such a change of the copper coordination geometry from the former to the latter produces a switching of the metal-based spin orbital and should lead to a significantly reduced coupling. In order to probe the crossover of the xy and z^2 spin orbital energies, we have performed EHMO calculations on the monomeric $[(NH_3)_4Cu(C_2O_4)]$ model system (see Figure 1). The bond distances, which are denoted as a, b, and c in

Table 3. Values of the structural parameters for selected steps in the hypothetical $[Cu(NH_3)_4(C_2O_4)]$ monomeric complex[a]

step	bond distance, Å		
	a	b	c
1	1.99	1.99	2.52
3	2.07	2.05	2.32
4	2.11	2.08	2.22
6	2.19	2.14	2.02
7	2.23	2.17	1.92

[a]Four nitrogen atoms from ammonia molecules and two oxygens from the oxalate group build the octahedral surrounding around the copper atom. The two nitrogens and the two oxalate oxygen atoms in trans positions are kept coplanar in the calculations.

Figure 1, are modified stepwise, the starting point (step 1 in Table 3) being close to the situation of the copper atoms in a (4+2) environment. The next steps are generated by adding the fixed amounts of $\Delta a=0.04$, $\Delta b=0.03$, and $\Delta c = -0.10$ per each step to the starting values in such way that step 6 reflects the real situation of the copper in a (2+4) geometry. The energy values of the xy and z^2 orbitals obtained from these calculations are plotted in Figure 2. In step 1, the octahedral e_g level split into xy and z^2 levels with the z^2 orbital being much deeper in energy. In the copper coordination geometry the unpaired electron on the metal center will be in the xy orbital. The energy gap between the two orbitals decreases as the octahedral compression increases. The crossover of the xy and z^2 orbital energies occurs at step 4 and the z^2 orbital describes the unpaired spin around each Cu(II) ion in the axially-compressed system.

The six-coordinate μ-oxalato-dicopper(II) complexes have been found with J values varying from approximately zero up to -400 cm^{-1} by the modification of the copper surrounding (see Table 2). In the copper dimers of a (4+2) octahedral coordination with four nearest neighbors in the basal plane, a strong antiferromagnetic coupling is explained as follows: the spin orbital for each Cu(II) ion is constructed from the xy orbital (referring to the reference axes shown in Figure 1) pointing toward the bridging and terminal ligands. The interaction of the two spin orbitals leads to two MOs, one symmetric (Ψ_S) and the other antisymmetric (Ψ_A) with regard to the mirror plane perpendicular to the $Cu_2(C_2O_4)$ network. These MOs are strongly antibonding with respect to the in-plane σ interactions of the metal xy orbitals with filled orbitals on the ligands (see Figure 3). This will result in the large energy gap Δe between the two MOs which is responsible for the strong antiferromagnetic coupling observed. In the dimers of a (2+4) octahedral coordination with two short Cu-N distances in axial positions, the principal lobes of the z^2 spin orbital for each Cu(II) ion are oriented along the axial nitrogen atoms. As shown in Figure 4, this orientation of the spin orbitals is unfavorable to propagate the exchange interaction between these two adjacent spins through the oxalate bridge due to its poor overlap, thereby decreasing the associated Δe value, in agreement with the very small coupling. The overlap integrals between the antisymmetric spin orbitals of the two
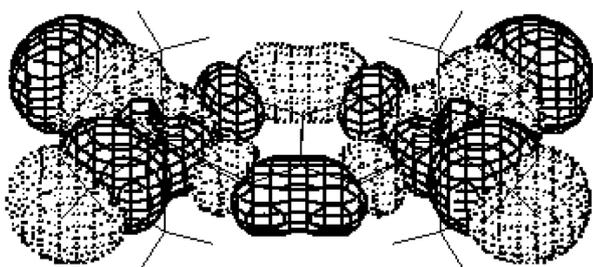
Figure 3. Schematic representation of the symmetric SOMO built from xy spin orbitals in [Cu(C$_2$O$_4$)(NH$_3$)$_4$], as calculated by the EH method.
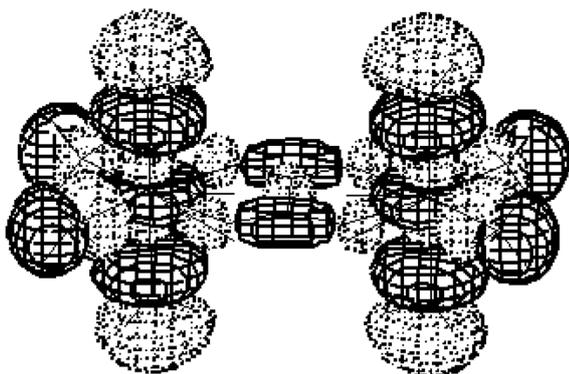
Figure 4. Schematic representation of the symmetric SOMO built from z^2 spin orbitals in [Cu(C$_2$O$_4$)(NH$_3$)$_4$], as calculated by the EH method.

magnetic centers and the bridge orbitals are −0.095 for the geometry of step 3 and −0.065 for that of step 4. The trend found for this magnitude is in agreement with that found for the energy gap between SOMOs showing a good correlation with observed J values (*vide infra*).

Calculations on hypothetic dimers described above give Δe = 233 meV with the mononuclear structure of step 3 and Δe = 67 meV with that of step 4. The energy gap Δe is 3.5 times larger for the former dimer than for the latter one. If we assume that in antiferromagnetically coupled systems, the variation of the experimentally observed J parameter is a good indication of the variation of J_{AF}, then we should expect the value of J reduced by a factor of $1/3.5^2$ for the (2+4) system. The trend appears fairly good in the observed J parameters given in Table 2. This result basically arises from the difference in magnitude of the overlap between the copper d orbital containing the unpaired electron and the bridging oxalate orbitals. In this qualitative scheme the explanation of the loss in exchange interaction would involve affirming that the xy spin orbital in the μ-oxalato copper(II) dimer is more efficient than the z^2 orbital in transmitting an exchange interaction through the oxalate σ molecular orbitals. A reversal of the spin orbitals due to the axial compression of the copper sites induces a drastic weakening of the antiferromagnetic coupling, so that the in-plane xy orbital makes up the predominant σ superexchange pathway in these compounds.

References

1. Hay, P. J.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1975**, *97*, 4884.
2. (a) Julve, M.; Verdaguer, M.; Kahn, O.; Gleizes, A.; Philoche-Levisalles, M. *Inorg. Chem.* **1983**, *22*, 368. (b) Julve, M.; Verdaguer, M.; Gleizes, A.; Philoche-Levisalles, M.; Kahn, O. *Inorg. Chem.* **1984**, *23*, 3808.
3. (a) Curtis, N. F.; McCormick, I. R. N.: Waters, T. N. *J. Chem. Soc., Dalton Trans.* **1973**, 1537. (b) Felthouse, T. R.; Laskowski, E. J.; Hendrickson, D. N. *Inorg. Chem.* **1977**, *16*, 1077. (c) Kansikas, J.; Pajunen, A. *Acta Crystallogr., Sect. B* **1980**, *36*, 2423. (d) Castro, I.; Faus, J.; Julve, M.; Mollar, M.; Monge, A.; Gutierrez-Puebla, E. *Inorg. Chim. Acta* **1989**, *161*, 97. (e) Castro, I.; Faus, J.; Julve, M.; Munoz, M. C.; Diaz, W.; Solans, X. *Inorg. Chim. Acta* **1991**, *179*, 59. (f) Castro, I.; Faus, J.; Julve, M.; Gleizes, A. *J. Chem. Soc., Dalton Trans.* **1991**, 1937. (g) Julve, M.; Faus, J.; Verdaguer, M.; Gleizes, A. *J. Am. Chem. Soc.* **1984**, *106*, 8306. (h) Bencini, A.; Fabretti, A. C.; Zanchini, C.; Zannini, P. *Inorg. Chem.* **1987**, *26*, 1445. (i) Soto, L.: Garcia, J.; Escriva, E.; Legros, J.-P.; Tuchagues, J.-P.; Dahan, F.: Fuertes, A. *Inorg. Chem.* **1989**, *28*, 3378. (j) Soto-Tuero, L.; Garcia-Lozano, J.; Escriva-Monto, E. E.; Beneto-Borja, M.; Dahan, F.: Tuchagues, J.-P.; Legros, J.-P. *J. Chem. Soc., Dalton Trans.* **1991**, 2619.
4. (a) Tang, J.; Gao, E.; Bu, W.; Liao, D.; Yan, S.; Jiang, Z.; Wang, G. *J. Mol. Struct.* **2000**, *525*, 271. (b) Cano, J.; Alemany, P.; Alvarez, S.; Verdaguer, M.; Ruiz, E. *Chem. Eur. J.* **1998**, *4*, 476. (c) Cabrero, J.; Amor, N. B.; de Graaf, C.; Illas, F.; Caballol, R. *J. Phys. Chem. A* **2000**, *104*, 9983. (d) Castillo, O.; Luque, A.; Lloret, F.; Roman, P. *Inorg. Chem. Commun.* **2001**, *4*, 350. (e) Smekal, Z.; Travnicek, Z.; Lloret, F.; Marek, J. *Polyhedron* **1999**, *18*, 2787. (f) Castillo, O.; Luque, A.; Roman, P.; Lloret, F.; Julve, M. *Inorg. Chem.* **2001**, *40*, 5526. (g) Castillo, O.; Luque, A.; Julve, M.; Lloret, F.; Roman, P. *Inorg. Chim. Acta* **2001**, *315*, 9.
5. (a) Curtis, N. F. *J. Chem. Soc. A* **1968**, 1584. (b) Duggan, D. M.; Barefield, E. K.; Hendrickson, D. N. *Inorg. Chem.* **1973**, *12*, 985. (c) Nonoyama, M.; Nonoyama, K. *J. Inorg. Nucl. Chem.* **1981**, *43*, 2567. (d) Nonoyama, K.; Ojima, H.; Ohki, K.; Nonoyama, M. *Inorg. Chim. Acta* **1980**, *41*, 155. (e) Tuero, L. S.; Garcia-Lozano, J.; Monto, E. E.; Borja, M. B.; Dahan, F.; Tuchagues, J.-P.; Legros, J. P. *J. Chem. Soc., Dalton Trans.* **1991**, 2619.
6. Castillo, O.; Muga, I.; Luque, A.; Gutierrez-Zorrilla, J. M.; Sertucha, J.; Vitoria, P.; Roman, P. *Polyhedron* **1999**, *18*, 1235.
7. Tuero, L. S.; Garcia-Lozano, J.; Monto, E. E.; Borja, M. B.; Dahun, F.; Tuchagues, J. P.; Legros, J. P. *J. Chem. Soc., Dalton Trans.* **1991**, 2619.
8. Vicente, R.; Escuer, A.; Ferretjans, J.; Stoeckli-Evans, H.; Solans, X.; Font-Bardia, M. *J. Chem. Soc., Dalton Trans.* **1997**, 167.
9. Zhang, L.; Bu, W.-M.; Yan, S.-P.; Jiang, Z.-H.; Liao, D.-Z.; Wang, G.-L. *Polyhedron* **2000**, *19*, 1105.
10. Calatayud, M. L.; Castro, I.; Sletten, J.; Lloret, F.; Julve, M. *Inorg. Chim. Acta* **2000**, *300-302*, 846.
11. Glerup, J.; Goodson, P. A.; Hodgson, D. J.; Michelsen, K. *Inorg. Chem.* **1995**, *34*, 6255.
12. Youngme, S.; van Albada, G. A.; Chaichit, N.; Gunnasoot, P.; Kongsaeree, P.; Mutikainen, I.; Roubeau, O.; Reedijk, J.; Turpeinen, U. *Inorg. Chim. Acta* **2003**, *353*, 119.
13. Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397.
14. Ren, J.; Liang, W.; Whangbo, M.-H. *Crystal and Electronic Structure Analysis Using CAESAR.*; North Carolina State University: Raleigh, NC, 1998.
15. Khan, O. *Molecular Magnetism*; VCH: New York, 1993.