How Photoelectron Spectroscopy and Quantum Chemical Studies Can Help Understanding the Magnetic Properties of Molecules: An Example from the Class of Cu(II)−Bis(oxamato) Complexes

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Nanometer thin films of nonsublimable multinuclear transition metal complexes were deposited on Si by means of spin coating to enable photoelectron spectroscopy studies. In combination with density functional theory calculations, photoelectron spectroscopy is applied to gain insight into the electronic and magnetic properties of the complexes.

Introduction

The exploitation of electronic and magnetic properties of molecule-based thin films is a highly promising field both at fundamental and application levels.[1] Potential applications range from spintronic devices and magneto-strictive sensors to magneto-optical data processing units.[2,3] Significant progress in tailoring the magnetic and electronic properties of molecules was already made,[4] and several methods were applied for the preparation of films with thicknesses in the range up to several 100 nm[5] (and references therein).

The chemical variety resulting from the flexibility of carbon chemistry is of major importance for development in this field. As an example, Cu(II)−bis(oxamato) complexes have been used, in view of their large structural variability, either as precursors[6,7] for the synthesis of multimetallic complexes (see, e.g., refs 8−10) or as building blocks for two- and three-dimensional magnetic networks[11] and single molecule magnets.[12,13]

The present work focuses on photoelectron spectroscopy (PES) studies of the dinuclear complex [Cu$_2$(opba)(pmdta)] (**1**) and the trinuclear complexes [Cu$_3$(obbo)(pmdta)$_2$(NO$_3$)](NO$_3$) (**2**) and [Cu$_3$(obbo)(tmeda)$_2$(NO$_3$)](NO$_3$) (**3**), where obbo = *N,N′-o*-benzyl-bis(oxamato), opba = *o*-phenylene-bis(oxamato), pmdta = *N,N,N′,N′′,N′′*-pentamethyldiethylenetriamine, and tmeda = *N,N,N′,N′*-tetramethylethylenediamine.[14−16] The Lewis formulas of the investigated complexes are shown in Figure 1. All three complexes consist of combinations of the following ligand entities [Cu(opba)]$^{2-}$, [Cu(obbo)]$^{2-}$, [Cu(tmeda)]$^{2+}$, and [Cu(pmdta)]$^{2+}$.

Recently, spin coating was used to prepare thick films (several tens of nanometers) of nonsublimable transition metal complexes, such as Cu(II)−bis(oxamato) complexes.[17] This method allows good control of the film thickness while preserving the molecular structure. In this work, films with a nominal thickness smaller than 10 nm were prepared for PES investigations.

The magnetic properties of the compounds **1**−**3** were already reported in the literature.[14,16] They exhibit an antiferromagnetic coupling between the transition metal centers, the strength of which is characterized by J values of −112 cm^{-1} (**1**), −111 cm^{-1} (**2**), and −363 cm^{-1} (**3**) (Table 1). Since **2** and **3** are asymmetric with respect to the central metal atom, two different J values are expected for each of these two complexes. However, it was not possible to extract this information from the temperature dependent magnetic susceptibility measurements, since the fit was not sufficiently sensitive for the approximation of two different J values.[14] This problem appears for many systems in the field of molecular magnetism, posing a serious obstacle for the basic microscopic understanding of super-exchange coupling phenomena. Here, the ability of PES to provide element and site specific information will be exploited to obtain a deeper insight in the magnetic properties.

Experimental Section

The spin coated thin films were prepared in a nitrogen flushed glovebox. The transition metal complexes were dissolved in acetone (1 mg/mL) and spin coated on Si with a rotation speed of 120 rotations per minute (rpm) for 1 min and afterward rotated to dryness at 1000 rpm. Afterward, the samples were heated to 80 °C for 30 min.

The X-ray photoemission spectroscopy (XPS) studies were performed under high vacuum conditions (5×10^{-9} mbar base pressure) with the Al K$_\alpha$ (1486.6 eV) emission line, with a total energy resolution of ∼0.9 eV.

Quantum chemical calculations were performed with the program package TURBOMOLE[18] using methods of the density functional theory by applying the B3-LYP hybrid functional[19] with def2-TZVP[20,21] basis sets for all atom types. The NO$_3^-$ counterions were neglected, and the charge of the dication was

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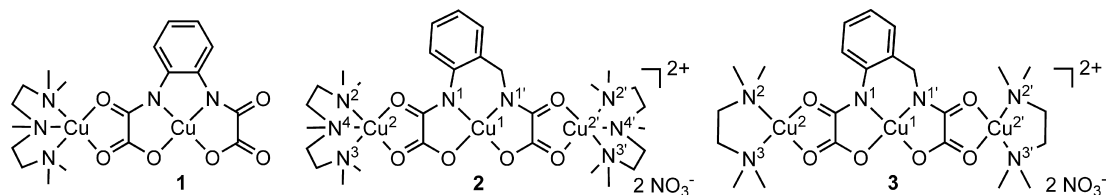|| Princeton University.

Figure 1. Lewis formulas of the compounds under investigation.

TABLE 1: Experimental (exptl) and DFT Calculated (calcd) *J* Values of 2 and 3

	exptl	calcd/cm^{-1}		calcd/1.5 cm^{-1}		
	J/cm^{-1}	J_{12}	$J_{12'}$	J_{12}	$J_{12'}$	$J_{12'}/J_{12}$
2	−111[15]	−165	−171	−110	−114	1.04
3	−363[15]	−554	−595	−369	−397	1.08

TABLE 2: Calculated Spin Population of 2 and 3

	Mulliken unpaired electrons			
	$\rho(Cu^1)$	$\rho(Cu^2)$	$\rho(Cu^{2'})$	$\rho(Cu^2)/\rho(Cu^{2'})$
2	0.5852	0.5442	0.5424	1.0033
3	0.5974	0.5499	0.5464	1.0064

TABLE 3: Hartree−Fock Orbital Energies for the 2p Orbitals of Cu^1, Cu^2, and Cu$^{2'}$ and the 1s Orbitals of N^1 to N^4 and N$^{1'}$ to N$^{4'}$ for Compounds 2 and 3 (The Values are Average Values of All Respective Orbitals at the Given Atoms)

compound **2**		compound **3**	
atom	energy/eV	atom	energy/eV
Cu^1	−975.20	Cu^1	−975.58
Cu^2	−976.01	Cu^2	−975.99
Cu$^{2'}$	−975.96	Cu^2	−975.83
N^1	−390.30	N^1	−390.56
N$^{1'}$	−390.05	N$^{1'}$	−390.32
N$^{2,2',3,3'}$	−391.20	N^{2,3}	−391.31
N$^{4,4'}$	−391.45	N$^{2',3'}$	−391.21

compensated by the conductor-like screening model (COSMO)[22] as in previous reports.[23,24] All calculations were done with default settings for convergence criteria and with default parameters for the COSMO model.

For the calculation of the magnetic coupling parameters, the broken-symmetry (BS) approach was used (for more details, see ref 5 and references therein).

Results and Discussion

Quantum Chemical Calculations of Magnetic Properties. It was previously shown[5] that the trends in *J* can be predicted with high accuracy for Cu(II)−bis(oxamato) complexes using the broken symmetry approach. The method and basis set used there predict properly the experimental trends, although the theoretical values are larger than the experimental ones.[5]

Since **2** and **3** have asymmetric *N,N′*-bridges with different spin densities on the nitrogen atoms bonded to the aryl and to the CH$_2$ group,[6] the J_{12}, between Cu^1 and Cu^2, and $J_{12'}$, between Cu^1 and Cu$^{2'}$, respectively, are intuitively expected to deviate from each other. From the magnetic susceptibility results, it was not possible to determine the exact values of the two different *J* parameters.[15] The *J* parameter of −111 cm^{-1}, roughly estimated from the experimental data, should be regarded as an average value of J_{12} and $J_{12'}$. The quantum chemical calculations of *J* yield indeed two values of *J* for the asymmetric complexes: $J_{12} = −165$ cm^{-1} and $J_{12'} = −171$ cm^{-1} for **2** and $J_{12} = −554$ cm^{-1} and $J_{12'} = −595$ cm^{-1} for **3**. The calculated values for **3** are much larger than those of **2**, in agreement with the experiment.[15] Previously, we have reported[5] for related Cu(II)−bis(oxamato)-type transition metal complexes that the theoretically predicted *J* parameters are about 1.5 times larger compared to the experimental values. After applying a correction factor of 1.5, the calculated values for **2** and **3** are close to the experimental results (see Table 1).

The calculated spin population on the Cu ions is summarized in Table 2. The spin population of the central Cu ion (Cu^1) is higher than that of the terminal Cu ions (Cu^2 and Cu$^{2'}$). The spin population on the Cu ions coordinated close to the aromatic (Cu^2) is slightly larger than that on the aliphatic part (Cu$^{2'}$) of the central ligand system. For **3**, the spin population on each of

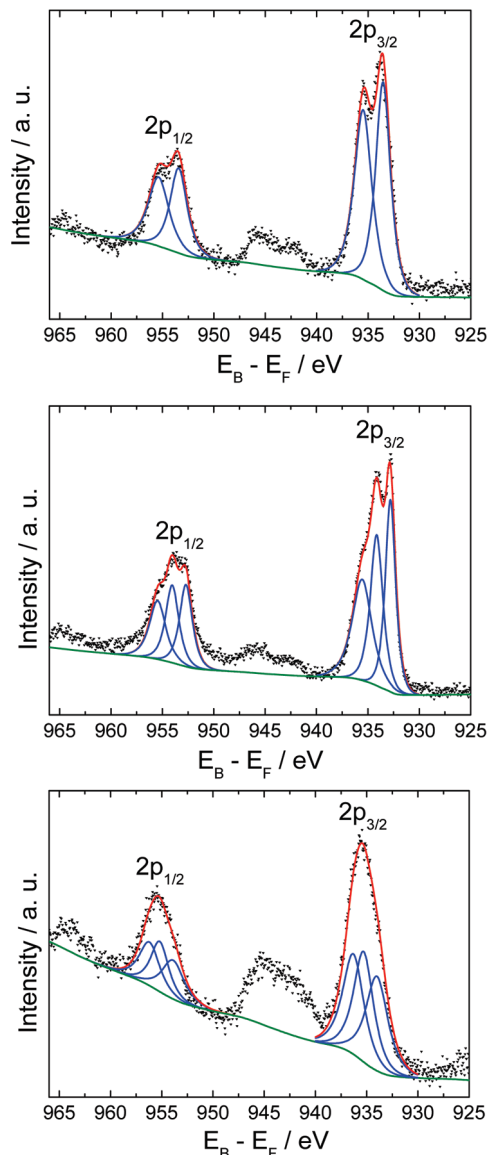the Cu ions is higher compared to **2**, leading to a larger *J* parameter for **3**.

Quantum Chemical Calculations of Electronic Properties. Binding energies (BEs) for electrons may be approximately identified with (negative) Hartree−Fock orbital energies (Koopman's theorem). This is usually done for energetically high-lying orbitals, but the approximation can also be applied for the core levels of, e.g., Cu 2p and N 1s when aiming to predict qualitatively trends rather than exact values of the binding energy. The BE of the Cu 2p and N 1s electrons calculated for compounds **2** and **3** are shown in Table 3 for the high-spin ground state case. For the low-spin ground state case, the BE of a given core level is identical for all atoms of the same element in the complex within the accuracy given in Table 3. The spin−orbit coupling was not considered in the calculations.

The data presented in Table 3 are average values of the alpha and beta N 1s orbital, and in the case of the Cu 2p orbitals average values of the alpha and beta p$_x$, p$_y$, and p$_z$ orbitals at each atom. The binding energy values of Cu are smaller for **2** than for **3**, a fact which is related to the different coordination geometries of the terminal ligand system (see Figure 1). While **2** has a trigonal bipyramidal coordination geometry, **3** has a distorted square planar coordination geometry, which is known to accommodate less electronic charge on the metal center, thus leading to a higher binding energy. This is in line with calculated average Cu 2p orbital energies for **2** and **3**, even if the difference is very small. More pronounced is the difference of Cu 2p orbital energies within one compound; for **2** it is larger than for 3**3**. This trend was also found for the experimental results and will be discussed below.

The calculated binding energies of the N 1s electrons on the central N atoms (N^1 and N$^{1'}$) are smaller than those of the terminal N atoms of the ligand, i.e., N$^{2,2',3,3',4,4'}$ for **2** and N$^{2,2',3,3'}$ for **3**, respectively. Again, this is in line with a larger amount of electronic charge at the respective N atoms: the partial charge on the central N atoms from NPA[25,26] amounts to ca. −0.80 and −0.83, whereas for the terminal N atoms a charge of −0.60 and −0.56 is calculated for **2** and **3**, respectively.

Photoelectron Spectroscopy Investigations. The Cu 2p core level spectra of the thin films of **1**, **2**, and **3** are shown in Figure

Letters

J. Phys. Chem. B, Vol. 113, No. 30, 2009 **10053**

Figure 2. XPS spectra of the Cu 2p core levels.

TABLE 4: XPS Fit Parameters for the Cu 2p Core Level Spectra of 1, 2, and 3 Shown in Figure 2

	atom	Cu 2p3/2		Cu 2p1/2	
		energy[a]	relative area	energy[a]	relative area
1	Cu^1	933.5	1	953.4	0.5
	Cu^2	935.5	1	955.4	0.5
2	Cu^1	932.8	1	952.7	0.5
	Cu^2	935.6	1	955.5	0.5
	$Cu^{2'}$	934.1	1	934.0	0.5
3	Cu^1	934.0	1	953.9	0.5
	Cu^2	936.3	1	956.2	0.5
	$Cu^{2'}$	935.3	1	955.2	0.5

[a] Error bars for the experimental fit: ±0.3 for **1** and **2**; ±0.6 for **3**.
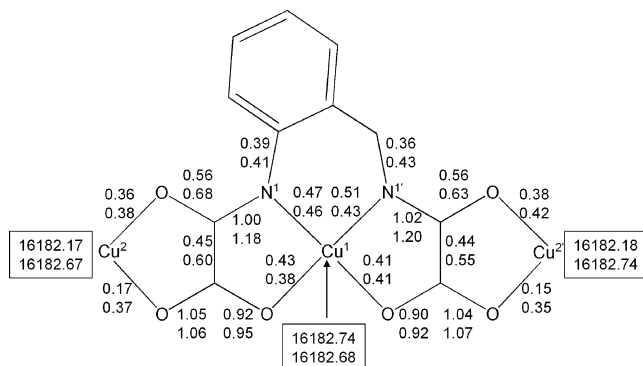
Figure 3. Total electron density at the position of the Cu nuclei (see numbers in boxes) and the Mulliken[26] overlap population given for **2** (upper number) and **3** (lower number).

theoretical predictions, the bands of **3** are shifted to higher binding energies compared to **2**, due to the different coordination geometry as outlined above. The differences in the binding energies of the three Cu ions in one compound are related to different spin and charge density distributions. The assignment of the bands in the PES spectra to the respective Cu atoms, outlined in Table 4, was based on the results of the quantum chemical studies discussed in the previous section.

The error bars for the experimental fit of **3** are slightly larger than those for **1** and **2** because the bands for the respective Cu(II) ions strongly overlap each other.

From magnetic susceptibility measurements, it is known that the *J* parameter of **3** is 250 cm^{-1} higher than the *J* parameter of **2**. This difference may be rationalized as follows: The pmdta ligands (3 N atoms) in **2** have a higher electron-pulling effect than the tmeda ligands (2 N atoms) in **3**. This has two consequences. On the one hand, the electron density is significantly decreased at the terminal Cu atoms in **2**, in particular the density at the nuclei; compare $\rho_n = 16182.17/$ 16182.18 (Cu2/Cu2′ in **2**) and $\rho_n = 16182.67/16182.74$ (for Cu2/ Cu2′ in **3**); cf. Figure 3. Accordingly, the nuclear charge is less well shielded, leading to lower orbital energies, i.e., higher electron binding energies. For the central Cu atom (Cu^1), the total density is very similar for **2** ($\rho_n = 16182.74$) and **3** ($\rho_n = 16182.68$). On the other hand, the presence of the electron-pulling pmdta ligand leads to a smaller overlap between Cu and the neighboring oxygen atoms, which results in a smaller coupling constant *J*.

The PES results in this work show that the binding energy of the Cu(II) ions in **3** is on average approximately 1 eV higher than that for **2**, indicating, for **3**, a stronger overlap of the orbitals of Cu with the ligand orbitals. This is in agreement with the results of the theoretical calculations that predict higher spin densities on the Cu ions in **3** compared to **2**. The Goodenough−

2. A Shirley-type background[27] has been subtracted from the spectra. The spectra consist of two spin−orbit components, which are both characterized by a main peak at lower binding energy and a satellite feature roughly 10 eV above. These arise from differently screened photoemission final states, and the latter is significantly broadened due to a final $2p^5 3d^9$ state multiplet.[28] Therefore, we use only the main peak for our analysis below. Selected parameters that have been used to fit the main line are summarized in Table 4. The decomposition of the Cu 2p core level emission assumes a spin−orbit splitting ($2p_{1/2}$ and $2p_{3/2}$) of 19.9 eV[29] and a statistical branching ratio of 1:2 for the p-levels.

For **1**, two bands at 933.5 and 935.5 eV can be clearly resolved. These two bands result from the two different coordination geometries, i.e., distorted square planar for the central Cu ion (Cu^1) and distorted trigonal bipyramidal for the terminal Cu ions (Cu^2). **2** and **3** contain three Cu ions. For the three Cu ions of each compound, different binding energies were theoretically predicted (Table 3) due to the asymmetry of the central *N,N′*-bridge with its nitrogens bounded to aliphatic and aromatic carbons. The experimental spectrum was therefore fitted with a set of three bands: 932.8, 934.1, and 935.6 eV for **2** and 934.0, 935.3, and 936.3 eV for **3**. In agreement with the

10054 *J. Phys. Chem. B, Vol. 113, No. 30, 2009*

Letters

Kanamori rules, experimentally demonstrated by, e.g., Crawford,[30] state that an increase of the magnetic orbital overlap yields an increase of the antiferromagnetic superexchange interaction.

Comparing the binding energies of the terminal Cu ions (Cu^2 and $Cu^{2'}$ in Table 4) within one complex, differences of 0.5 and 1 eV are found for complexes **2** and **3**, respectively. The fact that the binding energies of Cu^2 and $Cu^{2'}$ are not identical indicates slight differences in the bonding of the terminal Cu ions to the adjacent ligands, causing differences in the strength of the superexchange interaction (J_{12} and $J_{12'}$) to the central Cu^1 ion. The theoretical calculations also predict different J_{12} and $J_{12'}$ within one complex (see Table 1), and the predicted difference $\Delta J = J_{12} - J_{12'}$ is larger for **3** compared to **2**; i.e., it increases with the difference in the binding energy.

Although a quantitative relationship between BE and J cannot be provided in this work, our results show that PES can be used to determine whether if a different strength of magnetic superexchange coupling occurs in multimetallic magnetic molecules. This is of interest especially when this information cannot be extracted from temperature dependent magnetic susceptibility measurements.

Summary

Photoelectron spectroscopy in combination with density functional theory was shown to be a promising combination of methods to elucidate open questions in the interpretation of the magnetic behavior of molecules. The high sensitivity of photoelectron spectroscopy with respect to changes in the electronic structure of the molecule gives helpful information, especially when more than one magnetic superexchange interaction contributes to the magnetic behavior. For Cu(II)−bis(oxamato) complexes, the Cu $2p_{3/2}$ core level shifts to higher binding energy with increasing spin population on the Cu(II) ions, in the same manner as the previously reported increase of the antiferromagnetic superexchange interaction strength. Additional studies on a variety of complexes are necessary to derive a quantitative relation between the binding energies, spin population, and superexchange interaction strength.

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