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Shearing-Like Distortion in Binuclear End-to-End Cu^{II} Azido Compounds: An Ab Initio Study of the Magnetic Interactions

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The direct control of magnetic interactions in Cu^{II} azido-bridged binuclear complexes is investigated by means of explicitly correlated ab initio calculations. It is shown that in the end-to-end series, the shearing-like asymmetry parameter $\delta = d_{long}(Cu–N) – d_{short}(Cu–N)$ should be considered as an important parameter in the control of the coupling constant. A practical route that could be used to enhance the ferromagnetism of the compound is suggested in light of our calculations.

Introduction

The synthesis and characterization of magnetic systems such as fascinating single-molecule magnets (SMMs)[1] are of continuous interest. This particular activity stems from a simultaneous need for microscopic interpretations and the design of original materials. In particular, the demand for efficient information storage devices has stimulated the use of various metal centre types ranging from 3d to 4f ions.[1e] Meanwhile, the development of an effective magnetic coupler in binuclear systems has grown since the use of acetate groups.[2] In the Cu^{II} series, the magnetic interactions result from the presence of two unpaired electrons that give rise to the triplet (T) and singlet (S) states of energy difference $J = E_T – E_S$, where J is the traditional magnetic exchange coupling constant in a spin-only Heisenberg-type Hamiltonian $\hat{H} = –2J\hat{S}_1\hat{S}_2$. The intimate participation of the bridging moieties in the magnetic properties has been much investigated in the literature; an important manifestation is the so-called "noninnocent" ligands.[3] In this respect, the prediction of the magnetic properties in binuclear Cu^{II} compounds containing azide bridges remains a challenging issue. It is well-established that the azido group can bridge metal ions in two ways: the so-called end-on (EO) and end-to-end (EE) families (Figure 1). Nevertheless, the determination of the structural parameters that may control the magnetic interaction nature of the compounds is still much debated in the literature.[4,5] The general trend is that the EE mode affords antiferromagnetic interactions, whereas the EO mode favours ferromagnetic behaviour. However, the alternation of short and long Cu–N distances (so-called asymmetric coordination mode, see Figure 1) may result in either ferromagnetic or antiferromagnetic interactions whatever the coordination mode.[4] For symmetrically bridged compounds, theoretical investigations have rationalized the unequivocal distinction between the EO and EE families. Interestingly though, antiferromagnetic behaviour has been predicted in the EO series as soon as the Cu–N–Cu valence angle is sufficiently large (>104°),[6] which has also been experimentally confirmed.[7]

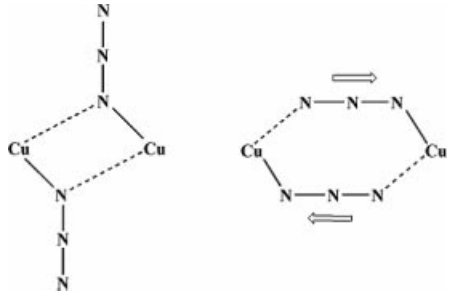

Figure 1. Asymmetric coordination modes of the azide bridge: EO (left) and EE (right). The arrows indicate the shearing distortion which is analyzed in this communication.

Magnetostructural correlations dedicated to EE compounds have pointed out that the symmetry of the coordination sphere measured by the Addison parameter (τ)[8] and the N–Cu···Cu–N torsion angle (Δ) are likely to govern the nature and strength of the magnetic interaction. Regarding the symmetry of the coordination sphere, it was proposed that in the square pyramid (sp) coordination limit ($\tau = 0$) magnetic orbitals are mainly $d_{x^2-y^2}$ and weak ferromagnetic

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Supporting information for this article is available on the WWW under http://www.eurjic.org or from the author.

interactions should result.[4c] Additionally, it was observed that large torsion angles Δ enhance ferromagnetic behaviour.[4c] Thus, considering the importance of azido-based clusters in the design of magnetic objects, we felt that the role of the coordination mode symmetry should be clarified. With the use of ab initio calculations, the contributions of spin polarization and dynamical correlation effects were analyzed in a series of EE complexes. The present works sheds light on another important structural parameter; the Cu–N bond length alternation. This particular shearing distortion mode acts as an electron-localizing factor in the eight-membered Cu–N rings of EE complexes. To clarify the role of the so-called shearing-mode, we used the crystal structure of a recently reported Cu^{II} azido complex.[9] We carried out the synthesis, structure and magnetic, polarized neutron of an asymmetric EE Cu^{II} azido complex $[Cu(L)(N_3)_2]_2$ [L = 7-(dimethylamino)-1,1,1-trifluoro-4-methyl-5-aza-3-hepten-2-onato] (**1**, Figure 2) that exhibits ferromagnetic interactions (J = 16 cm^{-1}) in contrast with most EE systems.[4] The strategy we developed consists of the systematic ab initio evaluation of the exchange coupling constant in a series of fictitious analogues of **1**. Therefore, starting from the experimental geometry for which ferromagnetism has been theoretically elucidated in our previous paper,[9] the Cu–N distances were modified whilst the rest of the complex was kept frozen (τ = 0.19 and Δ = 44.3). This particular approach differs from a previous study that focused on the long Cu–N distance;[5] here, we concentrated on the difference between the long and short Cu–N distances. This parameter we shall refer to as $\delta = \delta_{long}$(Cu–N) – δ_{short}(Cu–N) measures the amplitude of this shearing-like distortion away from a perfectly symmetric bridging mode. Let us mention that for δ = 0 Å, the Cu–N distances all equal 2.155 Å. Along this scheme, the Cu–Cu distance remains unchanged (5.1 Å). We then investigated the sensitivity of J with respect to δ in EE compounds reported in the literature.

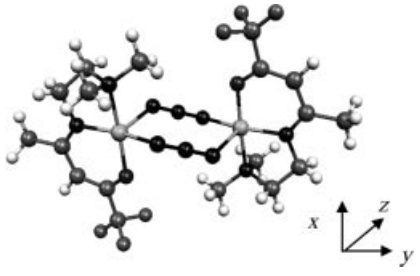

Figure 2. Structure of the EE $[Cu(N_3)L]_2$ compound with L = 7-(dimethylamino)-1,1,1-trifluoro-4-methyl-5-aza-3-hepten-2-onato.[9]

Theoretical Details

State-of-the-art ab initio, as well as density functional theory (DFT) calculations, proved to reach very satisfactory agreement with experimental measurements in both the EE and EO series. Nevertheless, correlated ab initio calculations were preferred here, as the information extracted from a multiconfigurational wavefunction is very insightful into the mechanism of magnetic interactions. First, complete active space self-consistent field calculations (CASSCF) including two electrons in two orbitals [CAS(2,2)] were performed by using the Molcas5.0 Package[10] to qualitatively incorporate the leading physical configurations. Because the local environments of the Cu^{2+} ions (d^9) are roughly ML_5, the singly occupied d-type orbitals are perpendicular to the missing ligand direction, which shall be referred to as z (see Figure 2). At this level, the low-lying triplet reads $|gu|$ where g and u are mainly the in-phase and out-of-phase linear combinations of the $d_{x^2-y^2}$ atomic orbitals, respectively (i.e. $g = \frac{a+b}{\sqrt{2}}$, $u = \frac{a-b}{\sqrt{2}}$, where a and b are the $d_{x^2-y^2}$AOs). Along this multiconfigurational scheme, the contributions of the so-called ionic forms $|a\bar{a}|$ and $|b\bar{b}|$in the ground-state singlet $\lambda|g\bar{g}| - \mu|u\bar{u}|$ may be underestimated. Thus, one has to incorporate dynamical correlation effects to fully account for the intimate mechanisms responsible for the singlet-triplet energy gap. By using the triplet molecular orbitals (MOs), dynamic correlation contributions were included with the difference dedicated configuration interaction (DDCI) method[11] implemented in the CASDI code[12] (see the Supporting Information for a detailed description of the computational procedure). This particular framework has provided very accurate results for these types of compounds and solid-state magnetic materials.[9,13]

Results and Discussion

Detailed analysis of the different contributions to the exchange magnetic coupling constant was given previously.[14] Therefore, we concentrated on: (1) the spin polarization (SP) effects, which are dominated by excitations involving the bridging-ligand orbitals and (2) the dynamical correlation (DC) effects that arise from the instantaneous polarization of the copper ions environments. By allowing specific excitations in the CI treatment, one can grasp selectively those effects and clarify the exchange coupling character. The variations in the J, SP and DC contributions as a function of δ are plotted in Figure 3.

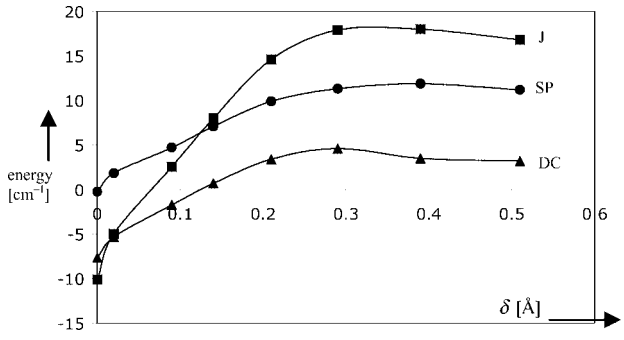

Figure 3. Calculated J (■), SP (●) and DC (▲) energies [cm^{-1}] in a series of **1** hypothetical analogues as a function of δ [Å].

As the asymmetry δ is increased (i.e. the Cu–N distances become significantly different), our calculated J values steadily increase to finally plateau close to 18 cm^{-1} for δ ca. 0.3 Å. This is in contrast to the dependence upon the long Cu–N distance for which no monotonic behaviour is observed (Supporting Information, Figure S1).

As previously reported,[14] the SP effects arise mainly from the polarization of the closed shells that are localized on the bridging units. As a result of the exchange operators $\hat{K}_a$ and $\hat{K}_b$, the closed shells h become polarized through $\langle p|K_a|h\rangle$ and $\langle p|K_b|h\rangle$ matrix elements involving virtual MOs p. The presence of a reflection plane makes the frontier MOs of the azido part h and p symmetric and antisymmetric, respectively (see Figure 4).

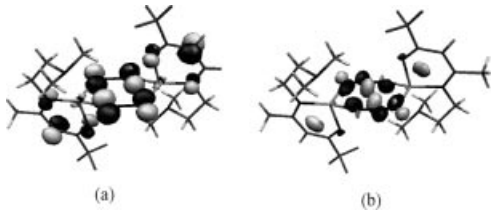

Figure 4. Frontier MOs (a) occupied h; (b) virtual p.

Thus, one can expect the SP contribution to be negligible, because the matrix elements are vanishingly small in the low-δ regime. As δ increases, a competition between the simultaneous shortening and lengthening of the Cu–N bond lengths results. Thus, the different copper–azido overlaps compete to reach a maximum, which fixes the SP contribution, which in turn favours the triplet state. Clearly, given the large Cu–Cu distance in the complex (≈ 5 Å), the contribution of the direct exchange is expected to be negligible.[13] A very similar behaviour for the DC effects is to be noticed. The DC contributions increase regularly with respect to the bridge shearing. The modification of the kinetic exchange only affects the singlet state because the ionic determinants are pure singlet and do not contribute to the triplet wavefunction. A detailed analysis of the wavefunction shows that the weights of these ionic forms is maximum, and still small, in the symmetric complex, i.e. for small δ values (Supporting Information, Table S1). Therefore, the singlet state is stabilized over the triplet and antiferromagnetic character results. One can intuitively expect the electron delocalization to be less efficient as the Cu–N bond lengths in the eight-membered ring alternate.

To investigate the role of the chemical environment of the copper atoms, we transformed the CF_3 electron-withdrawing groups into methyl groups. From our calculations performed at the same level, the magnetic coupling constant is 18 cm^{-1}, which is almost identical to the experimental and theoretical values reported for **1**.[9] Thus, one can take advantage of the structuring role of the CF_3 groups without greatly affecting the magnetic properties.

From this prospective analysis based on ab initio calculations, we finally examined whether magnetic behaviours could be anticipated in reported EE analogues. Table 1 summarizes the main structural parameters and experimentally determined coupling constants for some EE asymmetric azido-bridged complexes that are available in the literature.

We focused on pentacoordinate Cu compounds with only one exchange pathway. Figure 5 shows the variation of J with respect to both the dihedral angle Δ and shearing parameter δ. Even though the trend is not monotonous (see Figure 5), complexes with small δ values exhibit antiferromagnetic character (lower block in Figure 5), whereas ferromagnetic behaviour is exhibited as the shearing deformation increases (upper block in Figure 5). Strikingly though, complex **8** for which δ is relatively large displays antiferromagnetism. However, this compound presents a very asymmetric structure, with four different Cu–N distances. Moreover, the Cu–Cu distance as well as the τ value is significantly larger than that in all the other reported

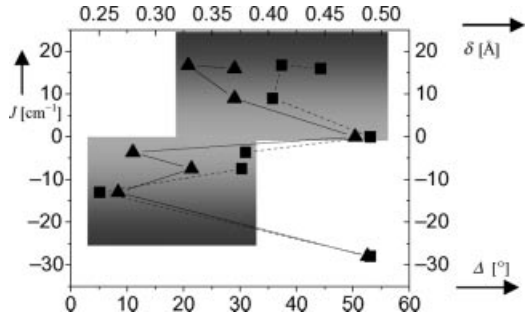

Figure 5. Variations of J with respect to Δ (■ dashed line) and δ (▲solid line).

Table 1. Structural and magnetic parameters for asymmetric Cu azido-bridged compounds.

Compound[a]	Cu–Cu [Å]	τ	Δ [°]	δ [Å]	J [cm^{-1}]	Ref.
1 $[Cu(L)(N_3)_2]_2$	5.073	0.19	44.3	0.370	16	[9]
2 $[Cu_2(bben)_2(N_3)_4]_n$	5.281	0.18	37.4	0.329	16.8	[4b]
3 $[Cu(Et_3dien)(N_3)_2]_2(ClO_4)_2$	5.407	0.20	35.8	0.370	9	[4c]
4 $[Cu(bp)(N_3)_2]_2(ClO_4)_2$	5.004	0.20	53.1	0.477	0	[4d]
5 $[Cu(EtMe_4dien)(N_3)_2]_2$	5.289	0.28	31.0	0.280	–3.6	[4e]
6 $[Cu(Me_5dien)(N_3)_2]_2(ClO_4)_2$	5.294	0.23	30.3	0.332	–7.5	[4e]
7 $[Cu(Me_5dien)(N_3)_2]_2(BPh_4)_2$	5.228	0.29	5.15	0.267	–13	[4f]
8 $[Cu(Et_5dien)(N_3)_2]_2(ClO_4)_2$[b]	5.464	0.43	53.1	0.488	–28	[4e]

[a] L = 7-(dimethylamino)-1,1,1-trifluoro-4-methyl-5-aza-3-hepten-2-onato, bben = 1,2-bis(benzylamino)ethane, Et_3dien = triethyldiethylenetriamine, bp = 2,2′-bipyridine, $EtMe_4dien$ = 4-ethyl-1,1,7,7-tetramethyldiethylenetriamine, Me_5dien = 1,1,4,7,7- pentamethyldiethylenetriamine, Et_5dien = 1,1,4,7,7-pentaethyldiethylenetriamine, Medpt = methyldipropylenetriamine. [b] Parameters calculated with average angles and bond lengths, as this compound exhibits two nonequivalent dimers.

compounds. Thus, from previous calculations one may expect a simultaneous reduction, though small, of the direct exchange contribution and an enhancement in the superexchange effects. The comparison of **8** with compound **4** is very instructive as the sets of parameters Δ and δ are very comparable. Therefore, the unexpected behaviour of **8** is completely attributable to the large τ value. Clearly, the magnetic behaviour is not strictly governed by a single structural parameter because important variations are observed around $\delta \approx 0.33$ Å (see compounds **4** and **6**).

Finally we looked into the variation of J with respect to Δ and our shearing parameter δ. Interestingly, these variations are similar (see Figure 5).

Whereas Δ concentrates on angular distortion, it is rather puzzling that δ, which takes into account the asymmetry of the coordination mode, can describe in a similar way the magnetic behaviour of such a system. This observation clearly deserves further investigation. One may suggest that in synthetic compounds any change in the torsion angle Δ can be a consequence of a variation of the shear δ value. From a structural analysis, these parameters cannot be completely independent. Therefore, one may expect a strong correlation between the variations of δ and Δ. The rationalization we have provided for the influence of this new parameter will call for more magnetostructural data, in particular in the field of single-chain magnets. However, our calculations in which we kept Δ frozen on purpose indicate that δ has a direct influence on the J value.

Conclusions

The δ parameter, which measures the shearing between the two azido bridges, strongly influences the magnetic behaviour of EE Cu^{II} compounds. The different leading contributions were analyzed by means of explicitly correlated calculations. We believe that magnetostructural correlations should include this particular parameter that turns out to be predictive. This work also suggests that specific magnetic properties can be tuned by varying δ on copper–azido magnetic prototype compounds. Undoubtedly, the versatility of the azide magnetic coupler arises from its ability to bind paramagnetic centres in various geometries.

Supporting Information (see footnote on the first page of this article): The theoretical framework that was used for the ab initio calculations, the xyz files (Angström) of the generated structures and the corresponding variations in the ionic over neutral forms in the singlet wavefunction. Variations in the J values in the reported systems are plotted as a function of the Cu–N long distance as proposed in ref.[5]

Acknowledgments

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