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Theoretical study on the magneto-structural correlation in imidazolate-bridged Cu(II) binuclear complexes

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A theoretical study on the magneto-structural correlation in binuclear Cu(II) complexes bridged by the imidazolate anion has been performed using the broken-symmetry approach with the framework of density functional theory (DFT). The calculated results show that the variational trends of the magnetic coupling constant J with geometrical parameters are different for two models. The magnetic coupling constant J mainly depends on the Cu–N–C(im) bond angle ϕ and is insensitive to the variation of the Cu–N(im) distance and the dihedral angle α between the bridged imidazolate ring and copper coordination planes. The dependence of J on the angle ϕ in the two models shows that the J values are equal when the Cu–N–C(im) angle $\phi \approx 128°$.

Introduction

Recently, much attention has been given to magneto-structural correlations in polynuclear systems to elucidate magnetic phenomena, design new molecular magnetic materials and to investigate the role of the polymetallic active sites in biological process.[1–9] These studies have shown that there are many factors affecting magnetic behavior, such as bond lengths, bond angles, dihedral angles, the trans or cis structures of bridging groups, and the different coordination environments of magnetic centers.[5–9] Based on this information, one can rationally design more effective models of biological processes or better molecular magnetic materials.

Imidazolate anion is known to act as a bridging ligand between copper(II) and zinc(II) in bovine erythrocyte superoxidant dismutase (BESOD).[10–16] In order to develop structural model compounds of BESOD, Lippard's group[17] and other groups[18–26] have synthesized and characterized a number of imidazolate-bridged di- and polynuclear copper(II) complexes. These studies have shown that the magnitude of the antiferromagnetic exchange strongly depends upon the geometry of the copper coordination, but only a few sporadic studies were devoted to the magneto-structural correlation for imidazolate-bridged coupling complexes.[27]

It has been demonstrated that the broken-symmetry approach, proposed by Noodleman, can offer an approximation to a limited configuration interaction and can be successfully applied to study the magnetic properties of binuclear compounds.[7–9] Hence, in our calculation, the broken-symmetry approach within the framework of density functional theory has been employed to investigate the dependence of the coupling constants on structural parameters and to analyze the magneto-structural correlation of imidazolate-bridged binuclear Cu(II) complexes.

Computational details

According to the Heisenberg model,[28] the Hamiltonian of the magnetic interaction between two paramagnetic ions can be written as $\mathbf{H} = -2JS_1{\cdot}S_2$; S_1 and S_2 stand for the spins of two metal ions and J is the magnetic coupling constant. A negative J value means antiferromagnetic behavior and a positive one means ferromagnetic behavior. By means of the model, the magnetic coupling constant for a Cu(II) binuclear system can be obtained from:

$$\mathrm{E(T)} - \mathrm{E(S)} = -2J \qquad (1)$$

where E(T) and E(S) represent the energies of the triplet and singlet states, respectively. However, it is difficult to calculate the energy of the singlet state accurately within one monodeterminant, since the energy gaps are very small among the low-energy singlet states in a weak coupling interaction.

To solve the problem in an approximate manner, a broken-symmetry (BS) wave function has been used to calculate the J value. This avoids the double inclusion of some contributions of the electronic correlation when DFT calculations are used. This method follows the proposal of Perdew, Savin and co-workers, who suggest that the broken-symmetry single determinant is the correct solution of the Kohn–Sham equations for single state.[29] In this paper, the BS state was used to substitute the pure singlet state to calculate the coupling constant J of Cu(II) binuclear complexes. So, eqn. (1) can be transformed into:

$$\mathrm{E(T)} - \mathrm{E(BS)} = -2J \qquad (2)$$

All the calculations have been performed using the Amsterdam density functional (ADF) package (version 2.0.1). Vosko, Wilk and Nusair's (VWN) functional was used for local spin density approximation (LSDA).[30] Generalized gradient correlations have been introduced by using the Becke exchange functional[31] and the Perdew correlation functional.[32] Four basis sets in ADF containing triple-ζ basis sets and a polarization function from H to Ar were used for all atoms in the systems. The frozen core (FC) approximation for the inner core electrons was employed. The orbitals up to 2p for Cu and 1s for C, N, O atoms were kept frozen. The scalar relativistic effect was taken into account. The convergence criterion of SCF was 10^{-6}. The numerical integration procedure applied for the calculation is the polyhedron method developed by Velde and co-workers.[33] All the calculations were done on an SGI O2100 server.

Experimental phenomena and model complexes

Table 1 lists the spin-exchange coupling constants and geometrical features for a variety of imidazolate-bridged copper

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Table 1 Magnetic coupling constant J and structural parameters for experimental compounds

Compounds[a]	r_1, r_2[b] /Å	ϕ_1, ϕ_2[c] /°	α_1, α_2[d] /°	R_{Cu-Cu}[e] /Å	Coordination number and geometry	J/cm^{-1}	Ref.
$[Cu_2(bpim)(im)]_2^{4+}$	1.992(1), 1.992(1)	144.8(3), 143.0(3)	4.7, 11.4	6.214(2)	4, square planar	−87.64(4)	17*g*
	1.972(1), 1.972(1)	125.5(3), 130.2(3)	98.2, 80.5	5.911(2)	4, square planar	−35.0(4)	
$[Cu_2(bpim)]^{3+}$	1.961(7), 1.966(7)	143.0(6), 142.2(7)	4.7, 11.4	6.137(2)	5, square pyramid	−81.8(5)	17*d*
$[Cu_2(Me_4bdpi)(H_2O)_2]^{3+}$	1.968(7), 1.973(8)	ND[f]	28.0, 28.0	6.197(2)	5, square pyramid	−36.7	23
$[Cu_2(pip)_2(im)]^{3+}$	ND[f]	120.0, 121.0	88.0, 88.0	5.93	4, square planar	−26.91(2)	17*a*
$[Cu_2(TMDT)_2(im)(ClO_4)_2]^{+}$	1.944(12), 1.966(14)	129.0(1), 129.0(1)	91.8, 90.0	5.935(4)	5, square pyramid	−25.80(16)	17*b*
$Cu_2(im)(L)^{3+}$	1.919(22), 1.984(22)	134.4(31), 129.1(29)	68.8, 79.1	5.99	4, square planar	−21.0	24*a*
$[Cu_2(Gly–GlyO)_2(im)]^{-}$	1.928(3), 1.940(3)	124.5(3), 124.1(3)	5.8, 10.4	5.800(1)	4, square planar	−19.0	18
$[Cu_2(Me_5dien)_2(biim)]^{2+}$	1.993(3), 2.324(3)[g]	111.6(2) (ave)	5.5, 5.5	5.489(1)	5, square pyramid	$\lvert J\rvert <$ *ca.* 0.5	19*b*

[a] Ligand abbreviations: bpim, 4,5-bis({[2-(2-pyridyl)ethyl]imino}methyl)imidazolate; im, imidazolate anion; Me$_4$bdpi, 4,5-bis[di(6-methyl-2-pyridymethyl)aminomethyl]imidazolate; pip, 2-({[2-(2-pyridy)ethyl]imino}methyl)pyridine; TMDT, 1,1,7,7-tetramethyldiethylenetriamine; L, 30-membered ('NO' core) macrocyclic; Gly–GlyO, glycylglycinate(2−); Me$_5$dien, 1,1,4,7,7-pentamethyldienthylenetriamine; biim, 2,2′-biimidazolate. [b] Cu–N(im) distance. [c] ϕ_1 and ϕ_2 are the Cu–N–C(im) angles (see text). [d] α_1 and α_2 are the dihedral angles between the bridging imidazolate ring and copper coordination planes. [e] Cu···Cu intramolecular distance. [f] Not determined in references. [g] Two values are both for r_1 and $r_1 = r_2$ in this compound.

compounds. The coordination geometry of copper(II) and the orientation of the imidazolate ring with respect to the copper(II) coordination plane vary considerably in these compounds. The structures of several of the compounds, determined by single-crystal X-ray diffraction, are shown in Fig. 1. All of the copper complexes exhibit an antiferromagnetic exchange interaction with J varying from almost 0 to −88 cm^{-1}. The mechanism of exchange interaction transmitted by a bridging imidazolate may occur through either the σ or π system of the bridging imidazolated ligand. In general, there is agreement that a superexchange pathway involving the π system is unlikely because of symmetry mismatch of the relevant ligand orbitals and the copper $d_{x^2-y^2}$ orbitals in the square planar or square pyramid geometries.[17] The representation for the σ-type superexchange interaction is sketched in Fig. 2.[19]

The extent of the coupling between the two copper ions depends on the overlap of the magnetic orbitals.[34] This, in turn, can be expected to depend on three factors: the metal-nitrogen [Cu–N(im)] distance, the Cu–N–C(im) angle ϕ, and the dihedral angle α between the bridging imidazolate ring and copper coordination planes. All these parameters are shown in Table 1 for the complexes for which structural and magnetic data are available. From Table 1 it is found that the Cu–N(im) distances show a fairly consistent variability, ranging from 1.919(22) to 1.993(3) Å. An increase in the Cu–N(im) distance should be expected to decrease the magnetic coupling interaction. However, from the data of Table 1 it seems to be the reverse, that is a longer distance is associated with a stronger coupling, which means that the order of the Cu–N(im) distance is the same as the order of the J value.

It has been suggested from experiments that the angles ϕ_1 and ϕ_2 in Fig. 2 are important in determining the J value. An increase in these angles is expected to produce stronger coupling. For example, $[Cu_2(bpim)]^{3+}$ has relatively large ϕ values (see Table 1) and the antiferromagnetic coupling is strong. The third parameter, α, varies from 4.7° to 98.2° throughout the series, and the compound with small α has large J value. Hence, it was speculated that there may be a dependence of the magnitude of the coupling constants J on the dihedral angle α. Perhaps both angles ϕ and α have a significant influence on the magnetic coupling interaction in the imidazolate-bridged binuclear copper(II) complexes. However, the overall correlation between J and ϕ or α is not good, suggesting that the ϕ or α angles alone do not determine the magnitude of J. To determine whether the structure parameters have a significant influence on the magnetic coupling interaction requires theoretical investigation of the magneto-structural correlations, which is difficult to do by experimental means.

To analyze the magneto-structural correlation, it is helpful to employ model structures because the goal of this work is

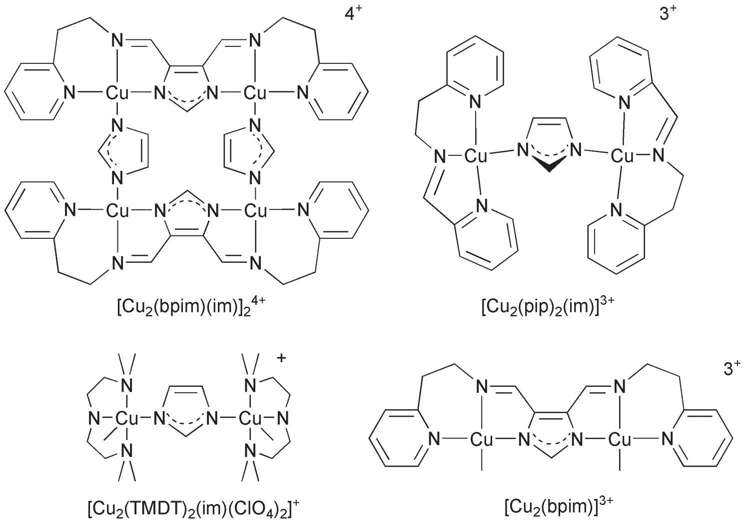
$[Cu_2(bpim)(im)]_2^{4+}$
$[Cu_2(pip)_2(im)]^{3+}$
$[Cu_2(TMDT)_2(im)(ClO_4)_2]^{+}$
$[Cu_2(bpim)]^{3+}$

Fig. 1 Structures of several imidazolate-bridged copper(II) compounds. Ligand abbreviations are given in footnote a of Table 1.

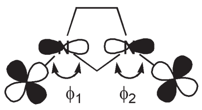

Fig. 2 Schematic representation of the magnetic orbitals for a Cu–im–Cu moiety.

to investigate the magneto-structural correlations theoretically. Experimentally, the magnetic susceptibility measurements are obtained from solid samples in which packing forces can produce small deviations from the structures of the isolated molecule. Hence, in our calculations, the model structures have been made as similar as possible to the corresponding part of the experimental structure. In most of the reported binuclear imidazolate-bridged copper(II) compounds the non-bridging ligands are amino and amide ligands or pyridines, hence, we use three amine ligands to coordinate each copper(II). Each copper(II) displays a square-planar coordination by three amines and a nitrogen atom from the imidazolate anion. As indicated in Fig. 1, there exist two structurally distinct classes. One has the imidazolate ring plane is nearly perpendicular to the copper coordination plane, which can rotate around the Cu–N bond. In the other class the imidazolate ligand is constrained in or nearly parallel to the copper coordination plane. So, in our paper, we use two models (a and b, see Fig. 3) to investigate the magneto-structural correlation in imidazolate-bridged binuclear copper(II) systems. The bond lengths and bond angles of model a and model b come from the perpendicular and parallel Cu-im-Cu moiety of complexes $[Cu_2(bpim)(im)]_2^{4+}$, respectively.

Results and discussion

Relationship between the dihedral angle *α* and magnetic coupling constant

Experimental results show that the magnitude of the coupling constant *J* for imidazolate-bridged binuclear copper(II) complexes depends on the dihedral angle α between the imidazolate ring and the copper coordination planes.[24] The smaller the dihedral angle α value, the stronger the antiferromagnetic coupling interaction, that is, the larger the *J* value. For example (see Table 1), a large *J* value ($-81.8\ cm^{-1}$) has been observed for compound $[Cu_2(bpim)]^{3+}$, which has small α values (4.7° and 11.4°). In contrast, the compound $[Cu_2(TMDT)_2(im)(ClO_4)_2]^+$ has relatively large α values (90.0° and 91.8°) and has a small *J* value ($-25.8\ cm^{-1}$). In order to investigate the effect of the dihedral angle α, using model a we let the dihedral angle α vary from 0° to 90° with an increment of 10°, and the calculated result is shown in Fig. 4. From Fig. 4, the *J* value decreases with increasing dihedral angle α, which is in good agreement with the experimental result that the *J* value of a compound with $\alpha \approx 0°$ is larger than that for a compound with $\alpha \approx 90°$. However, there is not a linear relationship between the dihedral angle α and *J*. Moreover, the coupling constant *J* is only changed by $\sim 3\ cm^{-1}$ as the dihedral angle α changes from 0° to 90°, indicating that the coupling constant *J* is relatively insensitive to variation of this angle. This is in opposition to what had been expected.

Relationship between Cu–N(im) distance and magnetic coupling constant

Keeping the Cu–N–C(im) angle at the average value in the perpendicular (model a) and parallel (model b) Cu–im–Cu moiety of $[Cu_2(bpim)(im)]_2^{4+}$, we changed the Cu–N bond distance from 1.94 to 2.01 Å with an increment of 0.1 Å. The energy for the broken-symmetry state as a function of Cu–N distance is shown in Fig. 5 and Fig. 6 for models a and b, respectively. In Fig. 5, the molecular energy firstly decreases and then increases with increasing Cu–N distance; the minimum is at ≈1.97 Å. This is consistent with the Cu–N bond length in the experimental compound $[Cu_2(bpim)(im)]_2^{4+}$, whose value is 1.972 Å. However, in Fig. 6, the molecular energy decreases as the Cu–N(im) distance increases in the range 1.94–2.01 Å. X-Ray studies of the structures of the complexes with the imidazolate ring plane being coplanar to the copper coordination plane show that the coordination sphere of the Cu^{II} ion is part of a five-membered chelate ring (see Fig. 1).

Generally speaking, short Cu–N(im) distances correspond to strong magnetic exchange interactions. To inspect the dependence of the exchange coupling interaction on the Cu–N(im) distance, the exchange coupling constant *J* is calculated as a function of Cu–N(im) distance and the results are shown in Fig. 7. It is found that the exchange coupling constants *J* obtained from model a are nearly constant and only changed by $\sim 1\ cm^{-1}$ as the Cu–N(im) distance varied from 1.94 to 2.01 Å. Therefore, when we explain the magnetic coupling interaction discrepancy for the compounds with $\alpha \approx 90°$ (model a), the influence of the Cu–N(im) distance can be neglected. For model b, the *J* value slightly decreases with increase of the Cu–N(im) distance, which is consistent with the result that an increase in the Cu–N(im) distance is expected to reduce the magnetic coupling constant. In addition, the $-J$ values (in cm^{-1}) are proportional to the following function of the Cu–N(im) distance, $-J = 416.96 - 172.64r$, where *r* is the Cu–N(im) distance in Å. The correlation coefficient is

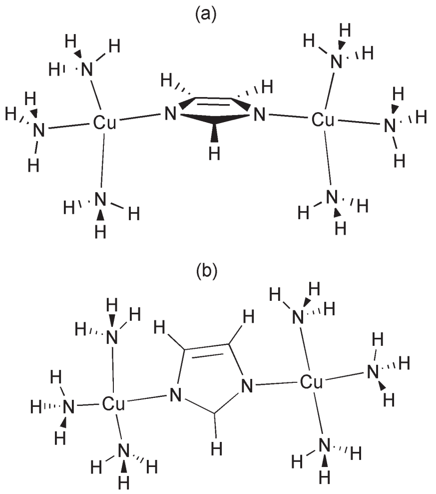

Fig. 3 Structures of the two models.

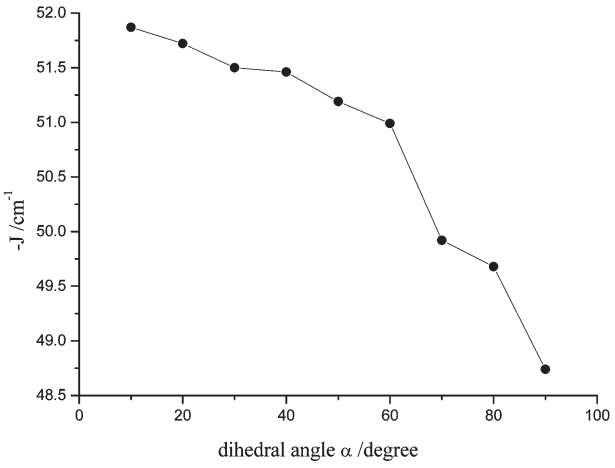

Fig. 4 Magnetic coupling constant *J* as a function of the dihedral angle α between the bridged imidazolate ring and copper coordination planes.

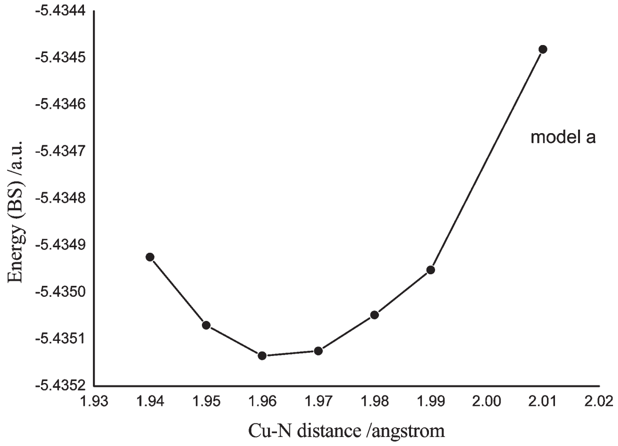

Fig. 5 Molecular energy of the broken-symmetry state for model a as a function of Cu–N(im) distance.

0.99996. Varying the Cu–N(im) distance by 0.07 Å, from 1.94 to 2.01 Å, results in a variation of 12 cm^{-1} for $-J$. The dependence of the exchange coupling constant on the Cu–N(im) distance suggests that the influence of this parameter should be considered when we explain the magnetic coupling interaction discrepancy for the compounds with $\alpha \approx 0°$ (model b). As a whole, the J value is insensitive to the Cu–N(im) distance for imidazolate-bridged Cu(II) dimers, although the J value shows a small decrease with increase of the Cu–N(im) distance. This result contrasts with the experimental phenomenon that the complexes with the largest antiferromagnetic coupling have the largest Cu–N(im) distance.

Relationship between Cu–N–C(im) angle ϕ and magnetic coupling constant

As the J value of the imidazolate-bridged Cu(II) compound with an angle $\phi = 111.6(2)°$ is observed to be almost 0 cm^{-1}, the bond angle ϕ was varied from 112° to 160° with an increment of 4°. The energy for the broken-symmetry state as a function of the bond angle ϕ is shown in Fig. 8. It is seen that the trends of the molecular energy variation with angle ϕ for model a and model b are similar to each other. The molecular energy decreases with increase of ϕ from 112° to 132°, passes through a minimum at $\phi \sim 132°$ and then increases for $\phi > 132°$. In other words, the imidazolate-bridged compound is most stable at $\phi \sim 132°$.

Fig. 9 depicts the dependence of the magnetic coupling constants J of model a and model b on the angle ϕ. In model a $-J$ increases rapidly as ϕ changes from 112° to 160°. For model b, the $-J$ value first decreases, then increases as ϕ is increased. It is noteworthy that the two curves have a crossing point at $\phi \approx 128°$, suggesting that the J values from the two models are equal when $\phi \approx 128°$ despite the other structural parameters. When ϕ is less than 128°, the calculated $-J$ from model a is smaller than the corresponding value of model b. While it is larger than 128°, the calculated $-J$ of model a is larger than that of model b. When the plane of the imidazolate ring is close to perpendicular to the copper coordination planes, as in model a, the average value of ϕ in experimental compounds is usually less than or equal to 128°. But for model b where the imidazolate ring plane is nearly coplanar to the copper coordination planes, the average angle ϕ in experimental compounds lies in the range from 112° to 145° and is often larger than 128°. Now, it is clear why the antiferromagnetic interactions observed for the experimentally known compounds with a dihedral angle α of around 90° are so much weaker than what is seen for the compounds with α around 0°.

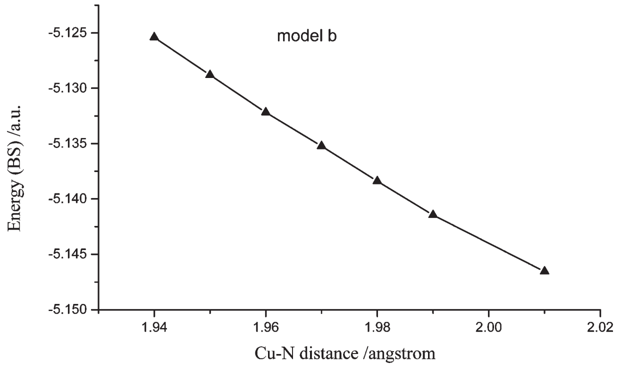

Fig. 6 Molecular energy of the broken-symmetry state for model b as a function of Cu–N(im) distance.

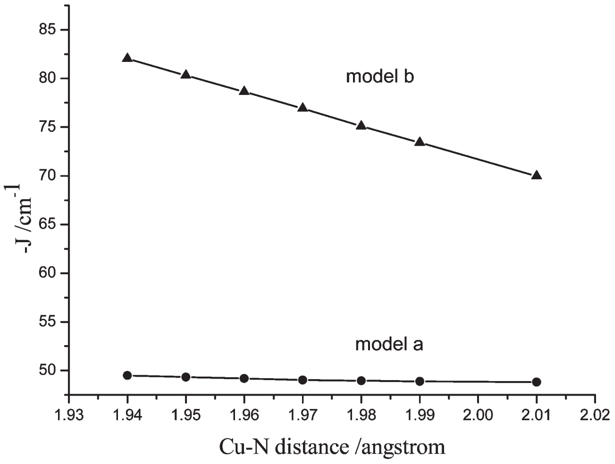

Fig. 7 Magnetic coupling constant J as a function of Cu–N(im) distance.

By comparing Fig. 7 with Fig. 9, it can be seen that changing ϕ from 112° to 160° results in a variation of 100 cm^{-1} in $-J$, while varying the Cu–N(im) distance from 1.94 to 2.01 Å results in a variation of only 12 cm^{-1} in $-J$. This indicates that the angle ϕ plays a key role in determining the magnitude of the magnetic coupling constant in imidazolate-bridged Cu(II) dimers, although the Cu–N(im) distance can affect the magnitude of the magnetic coupling constant. This can shed light on why the J value of $[Cu_2(bpim)]^{3+}$ is so much larger than that of $[Cu_2(Gly\text{-}GlyO)_2(im)]^-$. Although the Cu–N(im) distance in $[Cu_2(Gly\text{-}GlyO)_2(im)]^-$ is shorter than in $[Cu_2(bpim)]^{3+}$, the angle ϕ is larger in the latter than in the former. Since the influence of ϕ on the magnetic exchange interaction is more important than the Cu–N(im) distance, the J value of $[Cu_2(bpim)]^{3+}$ is much larger than that of $[Cu_2(Gly–GlyO)_2(im)]^-$.

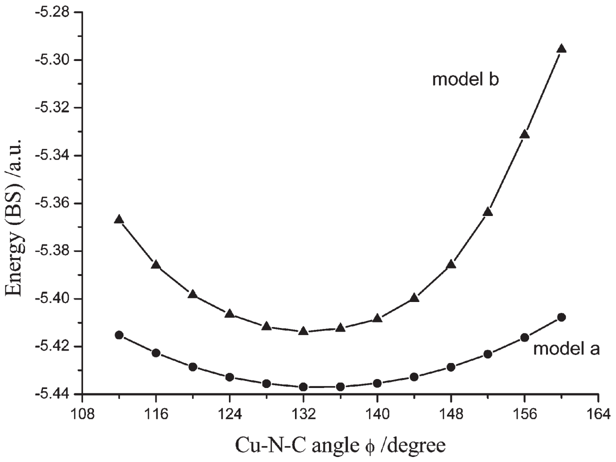

Fig. 8 Energy for broken-symmetry state as a function of the Cu–N–C(im) angle ϕ.

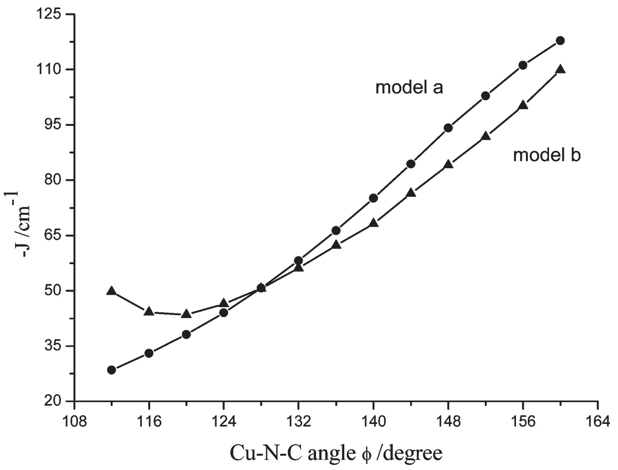

Fig. 9 Magnetic coupling constant J as a function of the Cu–N–C(im) angle ϕ .

Conclusions

The imidazolate-bridged binuclear Cu(II) complexes were studied using the broken-symmetry approach within the framework of density functional theory. Using two structurally different classes, the magneto-structural correlations for two models are explored in detail through changing the dihedral angle α between the bridged imidazolate ring plane and copper coordination planes, the Cu–N(im) distance and the Cu–N–C(im) bond angle ϕ. The calculated results show that the trends in the variation of magnetic coupling constants J with geometrical parameters are different. As a whole, J mainly depends on the bond angle ϕ and is insensitive to the dihedral angle α and the Cu–N(im) distance. The J values for the two models are equal at the angle $\phi \approx 128°$. The energy for the broken-symmetry state as a function of the angle ϕ shows that a minimum occurs at $\phi \approx 132°$.

Acknowledgements

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