

Theoretical studies of the spin states of macrocyclic aza-amido binuclear copper (II) complexes

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The spin and charge excitation gaps and charge and spin density distributions have been studied in macrocyclic binuclear aza-amido copper (II) complexes employing a model Hamiltonian. The spin gaps depend on the σ -orbital occupancies, and for small gaps, the exchange integral between the σ orbitals of the bridging oxygen atoms, K_{OO} , which is sensitive to geometry, determines the low-lying spin excitations. The singlet-singlet gaps also depend upon the σ -orbital occupancy but are weakly dependent upon K_{OO} .

1. Introduction

A large number of dinuclear copper complexes have been synthesized in the last two decades and their structure and magnetism have been extensively studied by different techniques [1-3]. Copper ions having one unpaired electron in the dimeric complex are subject to an effective exchange interaction whose strength and nature (ferromagnetic or antiferromagnetic) are determined by the structure and the participating ligands in the complex [4-7]. If the extent of interaction is in the intermediate range, NMR serves as an important tool and provides information such as spin excitation gaps and spin densities in the system [8]. The theoretical studies reported on these complexes have been very meagre and do not include a sufficient number of orbitals or electron configurations which are required to yield reasonable excitation gaps [9]. Ab initio calculations on such large systems would require including many orbitals as well as many configurations and would make the computations prohibitive [10]. The optimal choice appears to centre around a full-CI calculation of a model Hamiltonian that includes only the orbitals participating in the σ bonds between the copper ions and the ligand atoms. However, the parameters of such a model Hamiltonian must be well-characterized for the success of this approach. In the

case of copper ions, the recent surge of interest in the copper based high- T_c ceramic superconductors has led to a reasonable set of parameters for copper and the oxygen atoms which can serve as a starting point in any model calculation [11].

We have carried out some theoretical studies within the above approximation to understand the nature of the different spin states and the effect of the ligand orbitals surrounding the copper ions on the properties of these states. The theoretical calculations include the orbitals on the nearest-neighbours of the copper ions involved in σ -type of bonding with the $d_{x^2-y^2}$ orbitals of copper. Thus, we deal with a total of ten orbitals, and depending upon whether the nitrogen orbitals are participating in covalent or coordinate bonding, we have a total occupancy of 12, 14 or 16 electrons, corresponding to the three classes of complexes I, II and III that we deal with. The complete singlet manifold spanned in the case of III is 825 while with II it is 4950 and in I it is 13860. In the triplet case, these dimensionalities are, respectively, 990, 6930 and 20790, while the quintet dimensionalities for these systems are 210, 2310 and 8250. The theoretical calculations are carried out by employing a valence bond (VB) basis and using an interacting Hamiltonian that includes electron repulsions parametrically within the zero-differential-overlap (ZDO) approximation. The low-lying states

and their properties are obtained by solving the model Hamiltonian exactly to all orders in configuration interaction within this restricted basis. In conjugated as well as hetero-conjugated systems, such model Hamiltonians, after appropriate parametrization have yielded properties of low-lying states that are in very good agreement with experiments [12,13]. Furthermore, it has also been demonstrated that these parameters are transferable from one molecule to another. In reference to the parametrization of the properties of the copper d orbital, the range of these parameters is now reasonably well known [14]. Thus, it appears feasible to study the electronic states of the copper complexes in which the atom in the ligand bonding to the copper is nitrogen, oxygen or carbon in any hybridization.

Other important parameters in these type of systems are the metal–ligand–metal (M–L–M) bond angle, the metal–metal (M–M) distance and planarity of the complex [1,15]. It is experimentally known that the nature of the effective magnetic interaction depends on the M–L–M bond angle and that if the bond angle is greater than a critical bond angle (97.6°), the singlet will be the ground state, otherwise the ground state will be a triplet. It is also known that the strength of the interaction depends on the M–M distance and the interaction will be greater in planar complexes. Experimentally, these gaps can be followed by proton NMR or variable temperature magnetic susceptibility measurements [16]. In section 2 we describe the model Hamiltonian and the method of calculation, and in the last section we present a discussion of our results.

2. Model Hamiltonian and computational details

The many-body Hamiltonian that we deal with consists of orbitals on the adjacent atoms of copper ions involved in σ -type bonding with $d_{x^2-y^2}$ orbitals of the copper ions. The structure of the complexes and the orbitals taken into account are shown in fig. 1. We deal with a total of ten orbitals and 12 (fig. 1a), 14 (fig. 1b) or 16 (fig. 1c) electrons depending upon the nitrogen orbital occupancies. The Pariser–Parr–Pople (PPP) Hamiltonian over this orbital basis within the ZDO approximation in the second quantized notation is given by [17,18]

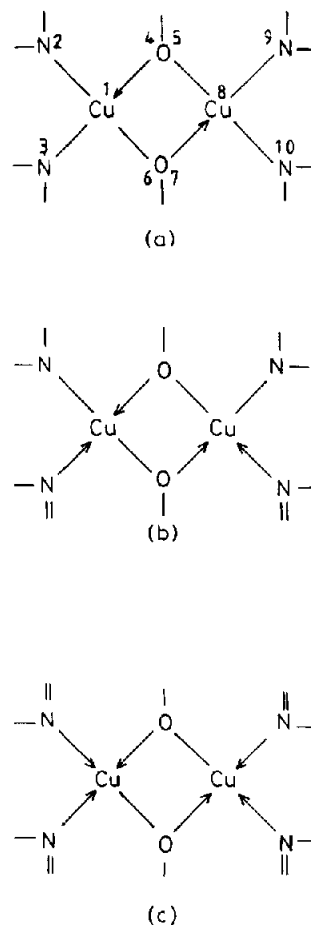


Fig. 1. Structure of (a) 12 electron, (b) 14 electron and (c) 16 electron complexes. The arrows indicate coordinate bonding. In the tables these complexes are referred to as I, II and III respectively.

$$\begin{aligned}
 H = & \sum_i \epsilon_i \hat{n}_i + \sum_{\langle ij \rangle} \sum_{\sigma} t_{ij} (a_{i\sigma}^* a_{j\sigma} + \text{h.c.}) \\
 & + \frac{1}{2} \sum_i U_i \hat{n}_i (\hat{n}_i - 1) + U_{\text{OO}} [(\hat{n}_4 - z_4)(\hat{n}_5 - z_5) \\
 & + (\hat{n}_6 - z_6)(\hat{n}_7 - z_7)] \\
 & + K_{\text{OO}} [(\hat{E}_{45} + \hat{E}_{54})^2 + (\hat{E}_{67} + \hat{E}_{76})^2 \\
 & - \hat{n}_4 - \hat{n}_5 - \hat{n}_6 - \hat{n}_7] \\
 & + \sum_{i>j} V_{ij} (\hat{n}_i - z_i)(\hat{n}_j - z_j), \quad (1)
 \end{aligned}$$

where ϵ_i is the site (orbital) energy of site (orbital) i , n_i is the occupation number operator for orbital i ,

t_{ij} is the transfer integral for the bond connecting adjacent atoms, $a_{i\sigma}^*$ ($a_{i\sigma}$) creates (annihilates) an electron with spin σ in the i th orbital and h.c. stands for Hermitian conjugate. The transfer integrals are set to 1.30 and 1.50 eV for the Cu–O and Cu–N bonds respectively. The value for the Cu–O bond at this distance has been established in the context of high- T_c superconductors and the Cu–N value is fixed taking into account the less compact orbitals of the nitrogen atom and the small difference in the Cu–N distance compared to the Cu–O distance. U_i is the electron repulsion integral between two electrons in the i th orbital and these values are reasonably well established for the $d_{x^2-y^2}$ orbitals as well as for the oxygen and nitrogen orbitals in different hybridizations. U_{OO} and K_{OO} are the Coulomb and exchange integrals involving two orbitals on the same oxygen atom. The optimal value for U_{OO} is 6.0 eV while that of K_{OO} is varied between 0.0 and -0.4 eV. The K_{OO} value will sensitively depend upon the hybridization of the oxygen orbitals and thus on the M–O–M angle. The operator $E_{ij} = (a_{i,\alpha}^* a_{j,\alpha} + a_{i,\beta}^* a_{j,\beta})$ is the electron transfer operator that hops an electron from orbital j to orbital i . V_{ij} is the interaction energy between an electron in orbital i on one atom and an electron on orbital j on another atom, and is parametrized following Ohno [19] as

$$V_{ij} = 14.397 \{ [28.794 / (U_i + U_j)]^2 + r_{ij}^2 \}^{-1/2}, \quad (2)$$

where z_i is the occupancy of the site i required to leave the site electrically neutral. The Ohno parametrization extrapolates the repulsion integral between U for $r_{ij} = 0$ and e^2/r_{ij} for large r_{ij} . The geometries of the complexes, necessary for calculating intersite interaction energies, are also shown in fig. 1. The values of parameters used in our calculations are given in table 1.

Table 1
Values of different parameters appearing in the PPP Hamiltonian in eq. (1). U_{OO} in eq. (1) is fixed at 6.0 eV while K_{OO} is varied from 0.0 to -0.4 eV. The σ orbitals on the primed atoms are doubly occupied

	N	N'	O	O'	Cu
ϵ	-1.0	-12.0	-2.0	-14.0	0.0
U	15.0	15.0	15.5	15.5	12.0
z	1	2	1	2	1

The PPP Hamiltonian (1) conserves total spin, and so we use a diagrammatic VB basis for obtaining the Hamiltonian matrix, the low-lying eigenvalues, charge densities and spin densities in the nonzero spin states by techniques described elsewhere [20,21].

3. Results and discussion

We have carried out calculations on the cluster of eight core atoms of the dinuclear copper complexes consisting of two bridge oxygen atoms and two nitrogen atoms bonding to each copper atom. We have considered only the σ orbitals on the ligand atoms that are bonded to the $d_{x^2-y^2}$ orbitals on the copper atoms. On the nitrogen atoms, these are approximately either sp^3 hybridized or sp^2 hybridized, depending upon the actual complex under consideration, while the oxygen orbitals are always nearly sp^3 hybridized. The $d_{x^2-y^2}$ orbital of the copper atoms contain one electron while the two hybridized oxygen orbitals on each atom participating in the bridge bonds together contain three electrons per oxygen atom. The nitrogen orbitals contain a varying number of electrons depending upon the hybridization on the orbital participating and the nature of the σ bond. If the nitrogen orbital is sp^2 hybridized then it is reasonable to expect the σ bonding with copper to be a coordinate bond and the associated sp^2 orbital will contribute two electrons. On the other hand, if the nitrogen is sp^3 hybridized, the σ bond to copper will be of the covalent type and the sp^3 nitrogen orbital will contribute one electron as can be seen from the structure of the complex. Thus the total number of σ electrons in the core of the complex actually depends on the hybridization on the nitrogen atoms and the type of Cu–N bond. The total occupancy in the ten orbitals can now be twelve (I), fourteen (II) or sixteen (III) depending upon the hybridization on the nitrogen atoms. If it is assumed that all the nitrogens are equivalent, the number of σ electrons in each nitrogen orbital is either one or two leading to I and III respectively. If, on the other hand, the two nitrogen atoms on the lower (or upper) half of the bridge are identical but differ from those on the other half, we will recover the case in which the number of electrons in the ten σ orbitals

is fourteen. Experimentally, II and III are known [1,22] while there seems to be no reason why I cannot be realized in the future.

The quantities we have studied theoretically are the energies of the low-lying singlet, triplet and quintet states and the charge and spin density (except in singlets where the spin density is identically zero) distributions in these states. We have studied these quantities for different values of the exchange integrals involving the two hybridized oxygen orbitals on the same atom. While we also considered two different sets of transfer integrals between all the bonded orbitals, one set corresponding to uniform transfer integrals (equal to 1.40 eV) and the other in which the copper–nitrogen transfer integrals are fixed at 1.50 eV and the copper–oxygen transfer integrals are fixed at 1.30 eV (to reflect the differences in bond lengths and atomic number in the two cases), we found that these sets gave very nearly the same energy gaps as well as other properties. Therefore, in what follows, we report results that correspond to uniform transfer integrals only. The molecular geometry of the complex enters the Hamiltonian via the intersite potential terms. In all cases, we assume the geometry to be the actual geometry obtained from the X-ray crystal structure studies of the binuclear copper(II) aza-amido macrocyclic complex. The values of all the other parameters except K_{OO} are held fixed at the values known from the literature from earlier studies [12–14]. These sets of parameters give the correct charge density distributions expected from basic valence arguments (table 2) and the spin gaps in the system are rather insensitive to small changes in these parameters as well as to small changes in the geometry of the complex. The parameter K_{OO} alters

the charge densities of the states by less than 1% for the range over which K_{OO} is varied.

Our calculations in these three cases with the model parameters fixed at the values in table 1 and $K_{OO}=0$ show that all three spin states are degenerate in I, the singlet and the triplet alone are degenerate and form the ground state in II and all three are nondegenerate in III with the singlet as the ground state (table 2). When a small negative K_{OO} is turned on, we find that ϵ_{ST} and ϵ_{SQ} (the singlet–triplet and singlet–quintet energy gaps respectively) vary linearly with K_{OO} and are highest at the highest absolute value of the parameter K_{OO} (table 3) in I. In II also ϵ_{ST} is small and increases linearly with K_{OO} but ϵ_{SQ} is large and insensitive to changes in K_{OO} . In III, both ϵ_{ST} and ϵ_{SQ} are rather large and nearly independent of K_{OO} (table 3). The large ϵ_{ST} and ϵ_{SQ} in III and the large ϵ_{SQ} in II are due to the fact that the electron delocalization is hindered in these complexes in the higher spin states. This is further supported by the charge density data on the three systems. In I, the charge densities in the different spin states are very nearly the same (table 2). The nearly identical charge densities in the different spin states reflect the small energy gaps between these states. In II, the charge densities in the singlet and the triplet states are very close but the charge density distributions in the quintet state are quite different (table 2). This explains the small singlet–triplet gap but a large singlet–quintet gap in II (table 3 and fig. 2). Indeed, recent experimental evidence on some of these complex moieties (II) indicates that ϵ_{ST} is of the order of 180–240 cm^{-1} [23]. In III, the charge density distributions in the singlet, triplet and the quintet states are quite different (table 2) and this is reflected in the large spin excitation gaps in the system (table 3). Thus,

Table 2

Charge densities at the different atoms in the complexes I, II and III, in singlet, triplet and quintet states for $K_{OO}=0.0$ eV. I, II and III denote the 12, 14 and 16 electron complexes, respectively

Atom	I			II			III		
	S=0	S=1	S=2	S=0	S=1	S=2	S=0	S=1	S=2
Cu	1.060	1.060	1.060	1.122	1.122	1.183	1.163	1.219	1.068
N	1.001	1.001	1.001	1.018	1.018	1.014	1.912	1.904	1.989
N'	1.001	1.001	1.001	1.892	1.892	1.860	1.912	1.904	1.989
O	2.939	2.939	2.939	2.968	2.968	2.944	3.012	2.973	2.955

Table 3

Energy gaps in cm^{-1} as a function of K_{OO} (eV) for a uniform transfer of 1.40 eV for all the bonds. I, II and III again denote the 12, 14 and 16 electron complexes, respectively

K_{OO}	I		II		III	
	ϵ_{ST}	ϵ_{SQ}	ϵ_{ST}	ϵ_{SQ}	ϵ_{ST}	ϵ_{SQ}
0.0	0	0	0	9830	6792	13370
-0.1	18	63	42	9770	6630	13230
-0.2	34	129	90	9770	6550	13070
-0.3	45	199	140	9770	6460	12920
-0.4	62	273	195	9770	6360	12770

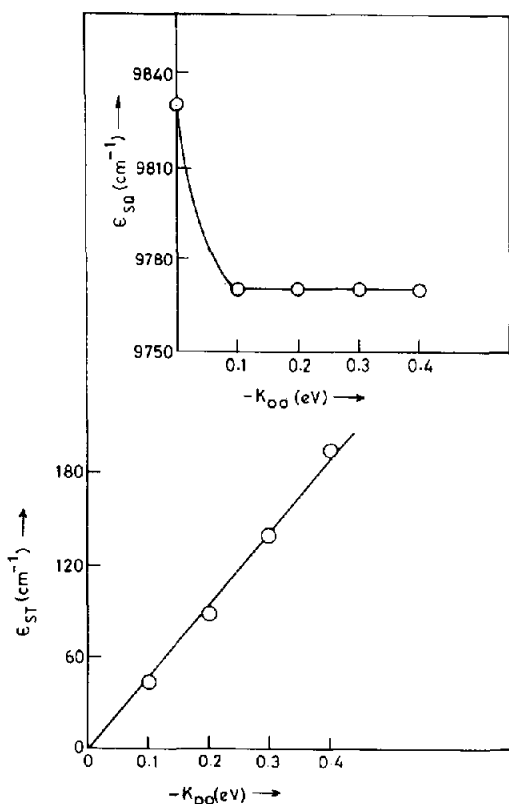


Fig. 2. Dependence of the singlet-triplet (ϵ_{ST}) and singlet-quintet (ϵ_{SQ}) energy gaps on K_{OO} in II.

if a spin excitation is accompanied by a large charge density redistribution, then the associated excitation gap is large and insensitive to the K_{OO} parameter. Otherwise, the spin excitation gap is small and depends sensitively on the value of K_{OO} . This is very similar to the two different types of excitations,

namely, the spin-wave and Stoner excitations in extended magnetic systems [24]. The spin-wave excitations are not associated with charge redistribution and form the low-energy excitation spectrum while the Stoner excitations which are of higher energy are particle-hole excitations and hence redistribute the charge density in the system.

It is interesting to compare the spin density distributions in these three complexes (table 4). In I, there is sizeable spin density on the terminal nitrogen atoms and the bridge oxygen atoms with a slight negative spin density on the copper atoms. In II, the spin density on the oxygen atoms and the nitrogens in the upper half (fig. 1b) are large and nearly equal while there is negligible spin density on the nitrogens in the lower half of the complex. The copper atoms have negative spin densities in this case as well. In III, the spin densities reside almost exclusively on the copper atoms and the bridge oxygen atoms and there are no negative spin density sites. The spin densities in the quintets are very nearly twice that in the triplets at all sites in I and III. In II, the large negative spin density on the copper in the triplet state changes to an equally large positive spin density in the quintet state while at the other sites, there is a slight increase in the spin densities in going from the triplet to the quintet state. The spin densities are insensitive to changes in the K_{OO} parameter just as the absolute energies of the different states. The marginal changes in the spin densities for different K_{OO} values are consistent with the slight changes in energies of the eigenstates with variation in this parameter. However, K_{OO} controls the spin excitation gaps completely, if the spin excitations do not significantly redistribute the charges, and we should expect

Table 4

Spin densities at the different atoms in the complexes I, II and III, in triplet and quintet states for $K_{OO}=0.0$ eV. The numbers in parentheses are the number of electrons in the cluster. Orbitals on the primed atom contribute two electrons

Atom	I(12)		II(14)		III(16)	
	S=1	S=2	S=1	S=2	S=1	S=2
Cu	-0.179	-0.358	-0.222	0.220	0.368	0.932
N	0.398	0.796	0.640	0.816	0.052	0.011
N'	0.398	0.796	-0.034	0.045	0.052	0.011
O	0.191	0.382	0.614	0.763	0.263	0.522

K_{OO} to be sensitive to the hybridization of the oxygen orbitals. The change in hybridization comes about from a change in the M-O-M bond angle and thus the latter is found to determine the nature and the strength of the effective exchange interaction.

The energy gaps between states of the same spin multiplicity have also been studied by us. Table 5 shows the variations in the singlet-singlet (ϵ_{SS}), triplet-triplet (ϵ_{TT}) and quintet-quintet (ϵ_{QQ}) gaps in these systems as a function of the exchange integral K_{OO} . In I, ϵ_{SS} increases slightly as K_{OO} is varied from 0 to -0.4 eV. The gap itself is small and lies between 0.75 and 0.8 eV. The gap ϵ_{TT} is about half ϵ_{SS} and since the lowest singlet and triplet are nearly degenerate, the second triplet also lies below the excited singlet state. The excited quintet state is well above the excited singlet state. However, in II, the excited singlet and excited triplet are nearly degenerate and are separated from the ground state by about 0.75 eV. In this case, both ϵ_{SS} and ϵ_{TT} decrease as K_{OO} is varied from 0 to -0.4 eV, although the magnitude of these changes is rather small. Both the lowest and the first excited quintet state are well above the ex-

cited singlet and triplet states, the gap ϵ_{QQ} is small and shows small increase with increase in K_{OO} . The spectrum in III is quite different (table 5). The first excited singlet state is slightly below the lowest quintet state while the second triplet state is below the excited singlet state. ϵ_{TT} is rather small while ϵ_{QQ} is ≈ 3.4 eV placing the second quintet state nearly 5 eV above the singlet ground state.

The above excitation gaps in the three complexes also depend weakly on the Cu-O and Cu-N transfer integrals, which in turn depend upon the geometry and the Cu-O and Cu-N distances. In table 6, we present these gaps for uniform and nonuniform transfer integrals for a typical value of K_{OO} . The gaps ϵ_{SS} and ϵ_{TT} show a decrease in going from uniform to nonuniform transfer integrals, while ϵ_{QQ} shows an increase, in I and III. The gap ϵ_{SS} is most sensitive to this change in transfer integrals since in singlets, the electron delocalization contributes more significantly to the energies. In II, the gaps ϵ_{SS} and ϵ_{TT} show a slight increase while ϵ_{QQ} shows a slight decrease, on introducing nonuniform transfer integrals.

To conclude, our exact solutions of the model

Table 5

Energy gaps in eV as a function of K_{OO} (eV) for a uniform transfer of 1.40 eV for all the bonds. I, II and III again denote the 12, 14 and 16 electron complexes, respectively

K_{OO}	I			II			III		
	ϵ_{SS}	ϵ_{TT}	ϵ_{QQ}	ϵ_{SS}	ϵ_{TT}	ϵ_{QQ}	ϵ_{SS}	ϵ_{TT}	ϵ_{QQ}
0.0	0.771	0.382	1.240	0.775	0.772	0.012	1.661	0.000	3.403
-0.1	0.765	0.384	1.238	0.764	0.766	0.033	1.623	0.020	3.416
-0.2	0.771	0.387	1.234	0.756	0.762	0.034	1.584	0.027	3.441
-0.3	0.779	0.391	1.229	0.747	0.758	0.035	1.546	0.036	3.440
-0.4	0.791	0.396	1.224	0.738	0.761	0.039	1.506	0.046	3.450

Table 6

Energy gaps in eV for $K_{\text{CO}} = -0.4$ eV with uniform transfers (A) for Cu-O and Cu-N bonds (both transfer integrals are set to 1.40 eV) and with nonuniform transfers (B) where transfer integrals for Cu-O and Cu-N bonds are set to 1.30 and 1.50 eV respectively. ϵ_{ST} , ϵ_{SQ} , ϵ_{SS} , ϵ_{TT} and ϵ_{QQ} denote the singlet-triplet, singlet-quintet, singlet-singlet, triplet-triplet and quintet-quintet energy gaps respectively

	I		II		III	
	A	B	A	B	A	B
ϵ_{ST}	0.008	0.007	0.024	0.031	0.789	0.688
ϵ_{SQ}	0.034	0.039	1.211	1.235	1.583	1.381
ϵ_{SS}	0.791	0.692	0.738	0.785	1.506	1.317
ϵ_{TT}	0.396	0.327	0.761	0.782	0.046	0.039
ϵ_{QQ}	1.224	1.266	0.039	0.028	3.450	3.584

Hamiltonians show that the spin excitation gaps in these dimeric copper complexes are almost entirely controlled by the exchange integral between the oxygen orbitals when the excitation gaps in the system are small. The geometry of the complex influences this parameter via change in hybridization of the oxygen orbitals involved in the bridging bonds. While other model parameters are also affected by the changes in geometry, these do not affect the energy ordering of the different spin states. The spin density distribution in the high spin states depends upon the number of electrons in the σ framework and the magnitudes of the spin densities are insensitive to the exchange integral between the orbitals on the bridge oxygen atoms. The energy gaps within the same spin manifold are different in the three systems and depend weakly on the Cu-O and Cu-N transfer integrals.

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