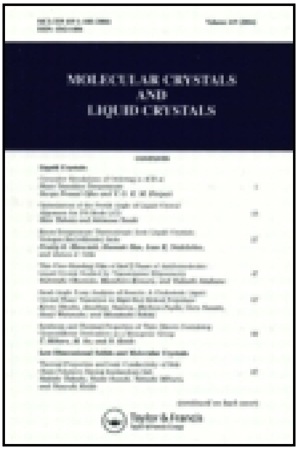

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Molecular Structure And Magnetic Characterization Of Structurally Reinforced Chiral Macrocyclic Poly- Amine-Based Dinuclear Copper(II) Complexes by x- and w- band ESR Spectroscopy and Squid Measurements

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MOLECULAR STRUCTURE AND MAGNETIC CHARACTERIZATION OF STRUCTURALLY REINFORCED CHIRAL MACROCYCLIC POLYAMINE-BASED DINUCLEAR COPPER(II) COMPLEXES BY X- AND W-BAND ESR SPECTROSCOPY AND SQUID MEASUREMENTS

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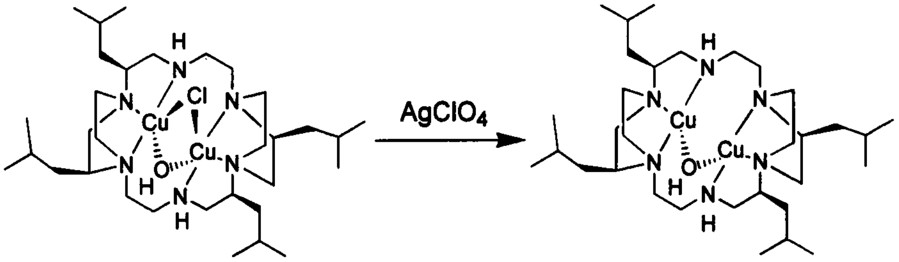
Abstract An attempt has been made to synthesize structurally reinforced chiral B_2-18-membered hexaazamacrocyclic amine based dinuclear copper(II) complexes **2** and **2'** as models for studying the size-match selectivity of metal ions. These two dinuclear complexes have manifested a prominent difference in the electronic spin structure, although only apparent structural difference is subtle. The complex **2** is double-bridged with an oxygen and chloride atom while **2'** is single-bridged only with the oxygen atom of hydroxide ion and the fifth ligand Cl is missing. From cw ESR measurements of **2** and **2'** in polycrystalline solids a large zero-field splitting (ZFS) value has been determined for **2'**and a small ZFS value for **2**, respectively. These findings have been in accordance with the results from the SQUID measurements. The ZFS values and isotropic exchange interaction have been theoretically estimated on the basis of molecular structural considerations of the complexes. The ground-state spin structures for the complexes **2** and **2'** have been discussed in connection with the geometry of the bridging oxygen linker.

INTRODUCTION

Structurally reinforced saturated polyazamacrocyclic molecules have drawn considerable attention, since the bridging of adjacent secondary amino groups in the macrocycle as a ligand provides us with a facile method for controlling the propensity of the polyazacycle for binding to a single metal ion or multiple ones in folded (cis) molecular conformations. From the viewpoint of molecularly based magnetism-structure relationship, the molecular structural constraint by the reinforcement is of crucial importance in order to control spin alignment in intramolecularly multiple nuclear metal ionic systems.

For the purposes of studying the size-match selectivity of metal ions and subtle influence of the geometry of metal binding sites on the spin alignment in dinuclear systems, an attempt has been made to synthesize structurally reinforced chiral B_2-18-membered hexaazamacrocyclic amine based dinuclear copper(II) complexes **2**and **2'** (see Figure 1). X-ray diffraction analyses[1] have shown that the dinuclear copper(II) complex **2** is joint square bipyramidal with a single common ridge line Cl1-01 and copper(II) lies nearly in each square plane, where Cl1 is a single axial ligand, as depicted in Figure 2. The macrocyclic cavity is rugbyball-shaped.[1] In the complex **2'** the remote linker as the fifth ligand Cl1 in **2** is missing, forming slanting disjoint bi-squares with a single common O1 of hydroxide ion. The geometry of the metal-binding site in **2'** is subject to a subtle change because of the missing ligand Cl1, leading to a change in exchange interaction between the two copper(II) ion. Only the ORTEP view of the metal-binding site is shown in Figure 2 with nuclear distances.



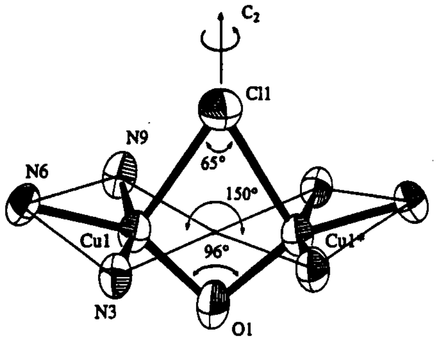
2 **2'**

FIGURE 1 Structurally reinforced chiral B_2-18-membered hexaazamacrocyclic amine based dinuclear copper(II) complexes **2** and **2'**. Note that the fifth ligand Cl in **2** is removed by $AgClO_4$.

MOLECULAR STRUCTURE OF JOINT BIPYRANIDS OF 2

The nuclear distance between the two copper(II), R(Cu1-Cu1*) is 2.83Å. They are not remote, but close enough to undergo exchange coupling of the two unpaired electrons each of which occupies a 3d orbital of copper(II) ion. R(Cu-N) ranges from 2.00 to

2.05Å and (Rcu-O1) = 1.91Å. The distance between Cu1(or Cu1*) and Cl1 is 2.65Å, showing that Cl1 is far remote, compared with R(Cu-N). The dihedral angle between the planes, N3N6N9 and N3*N6*N9* is approximately 150°. The angle between Cu1O1 and Cu1*O1 is 96°, which effects the occurrence of superexchange interaction via the oxygen atom O1. Thus, the local geometry of the metal binding site influences electron spin alignment between the two copper(II). The C_2 symmetry axis is along the common ridge line Cl1-O1 as shown in Figure 2.



Distances (Å)	
Cu1-Cu1*	2.832(3)
Cu1-Cl1	2.647(2)
Cu1-O1	1.908(7)
Cu1-N3	2.050(5)
Cu1-N6	1.999(6)
Cu1-N9	1.999(6)

FIGURE 2 ORTEP view and local geometry of the metal binding site in **2**.

EXPERIMENTAL

The details of the syntheses of **2** and **2'** will be published elsewhere. Only the final stage is given in Figure 3 and Figure 1 for **2** and **2'**, respectively. Single crystals of **2** were obtained from water solution. The details of the molecular structure and the molecular packing will be described elsewhere.[1]

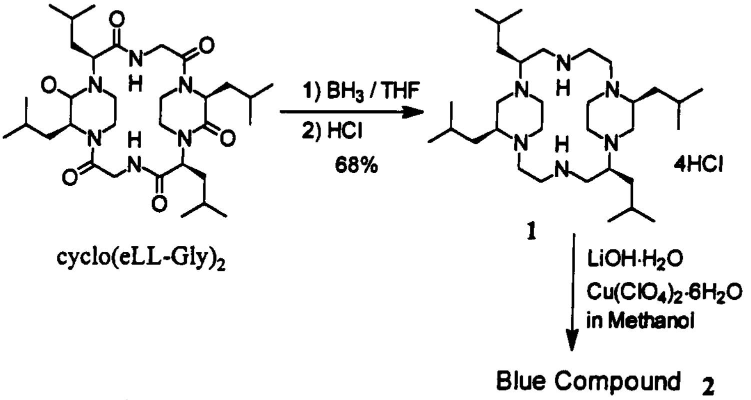


FIGURE 3 Synthetic route of the dinuclear complex **2**.

ESR measurements have been made with a Bruker ESP 300 spectrometer (X-band) equipped with an Oxford helium-gas flow variable temperature controller ESR910. High-field W-band fine-structure spectra of **2'** have been measured at ambient temperature. Magnetic characterization of **2** and **2'** has been made in parallel by means of Quantum Design SQUID magnetometers.

RESULTS AND DISCUSSION

Figure 4 shows a powder-pattern ESR spectrum of **2** in polycrystalline solid observed at room temperature. The spectrum is characteristic of an exchange-coupled pair of the electrons localized on the copper(II) ions, revealing that the copper hyperfine structure is smeared out and only a residual g-anisotropy remains. The spectrum essentially consists of fine structure attributable to a triplet state with relatively small ZFS parameters. The temperature variation of the observed spectrum was indicative that the triplet state lies thermally accessible above the singlet ground state. With decreasing temperature

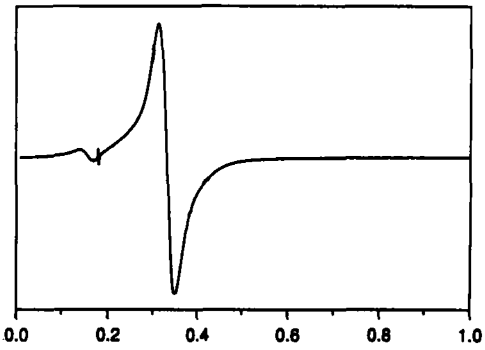


FIGURE 4 Powder-pattern fine-structure ESR spectrum of **2** in polycrystalline solid observed at 3.7K.

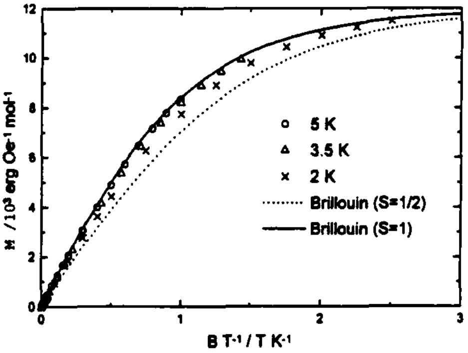


FIGURE 5 Magnetic curve of **2** in polycrystalline solid.

down to 3K, the signal intensity increased without lineshape change observed. The singlet-triplet energy gap was estimated to be ~ 2×10^{-4} cm^{-1}. Magnetic susceptibility measurements with the SQUID magnetometers were also indicative of the thermally accessible triplet state with a small singlet-triplet energy gap, as shown in Figure 5. High-field W-band ESR measurements are under way in order to locate the triplet state with good accuracy.

On the other hand, typical powder-pattern fine-structure spectra with some of the features of the triplet state have been observed from **2'** in the wide range of 300 to 2.8K, as shown in Figure 6. The spectrum in Figure 6 is characteristic of the triplet state with a large ZFS parameter D and considerable departure from axial symmetry. It turns out that the linewidth of a single transition exceeds 50 mT with anisotropic variation. Spectral simulation based on the eigenfield method [3,4,5,6] has allowed us to extract ZFS parameters ($|D|=0.30$ cm^{-1}, $|E|=0.018$ cm^{-1}) and anisotropic g values ($g_x=2.20$, $g_y=2.10$, $g_z=2.00$). In order to determine the absolute sign of the D value, high-field W-band ESR measurements are under way. The temperature variation of the fine-structure spectra from **2'** has been indicative of the thermally accessible triplet state. Precise ESR signal intensity measurements with elaborate temperature calibration using an internal standard are in progress as well as SQUID measurements.

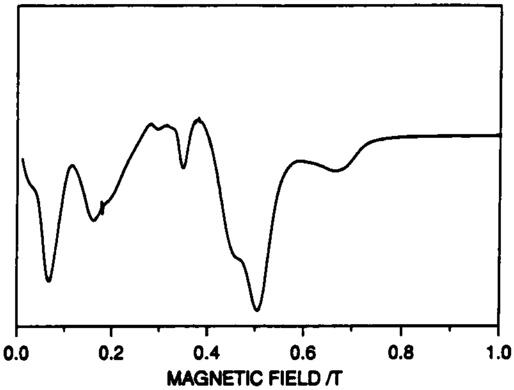


FIGURE 6 Powder-pattern fine-structure ESR spectrum of **2'** (Cl mising) in polycrystalline solid observed at 3.3K.

Magnetic Dipolar Interaction Model

In order to examine spin alignment mechanisms in the dinuclear complex **2'**, we have employed a theoretical model based on magnetic dipolar interaction with g-anisotropy taken into account, assuming that the distance R(Cu1-Cu1*) and the geometry of the metal-binding site in **2'** are similar to those in **2**; the dihedral angle is assumed to be 180° in stead of 150°.

Assume that the spin state under study is orbitally nondegenerate, then the interaction between the two spins can be expressed by the Hamiltonian

$$H = \tilde{\mathbf{S}}_{\mathbf{A}} \bullet \mathbf{J}_{\mathbf{AB}} \bullet \mathbf{S}_{\mathbf{B}}$$

where $\mathbf{S}_{\mathbf{A}}$ and $\mathbf{S}_{\mathbf{B}}$ stand for the effective spin operators corresponding to two centers A and B. $\mathbf{J}_{\mathbf{AB}}$ is a second-rank tensor containing exchange interaction parameters as functions of the distance between the two centers and their molecular structural geometries. $\mathbf{J}_{\mathbf{AB}}$ is decomposed into the sum of a symmetric and asymmetric part. The former gives an isotropic energy J and the latter is an anisotropic tensor $\mathbf{D}_{\mathbf{AB}}{}^{\mathrm{dip}}$, giving ZFS parameters due to the magnetic dipolar interaction.

The classical expression for the dipolar interaction energy between the two spins separated by a distance r can be given as

$$U_{\mathrm{dipolar}}\,(\mathbf{r}) = (\mu_0/4\pi r^3)[\tilde{\mathbf{m}}_{\mathbf{A}} \bullet \mathbf{m}_{\mathbf{B}} - 3(\tilde{\mathbf{m}}_{\mathbf{A}} \bullet \mathbf{r})(\tilde{\mathbf{r}} \bullet \mathbf{m}_{\mathbf{B}})]$$

where **r** represent the unit vector joining the two spins. Vectors $\mathbf{m}_{\mathbf{A}}$ and $\mathbf{m}_{\mathbf{B}}$ are the classical magnetic moments. In terms of a quantum-mechanical description, the magnetic moments are replaced by the spin operators. For a system with the g anisotropy, the magnetic moment can be shown to be

$$\mathbf{m} = -\,\beta\tilde{\mathbf{g}} \bullet \mathbf{S}$$

where **g** is the **g** tensor for the effective spin. Assume that the interacting spins $\mathbf{S}_{\mathbf{A}}$ and $\mathbf{S}_{\mathbf{B}}$ are sufficiently separated at some distance larger than ~ 2Å, then the magnetic interaction can be approximated to be the magnetic dipolar interaction. The dipolar interaction H is expressed as

$$H = \tilde{\mathbf{S}}_{\mathbf{A}} \bullet \mathbf{J}_{\mathbf{AB}}{}^{\mathrm{dip}} \bullet \mathbf{S}_{\mathbf{B}}$$

where

$$\mathbf{J}_{\mathbf{AB}}{}^{\mathrm{dip}} = (\beta^2/r^3)[\tilde{\mathbf{g}}_{\mathbf{A}}\bullet\mathbf{g}_{\mathbf{B}} - 3(\tilde{\mathbf{g}}_{\mathbf{A}}\bullet\mathbf{r})(\tilde{\mathbf{r}}\bullet\mathbf{g}_{\mathbf{B}})]$$

and note the change of units. Using the polar angles θ and φ, $\mathbf{r}$ is given by

$$\mathbf{r} = \mathbf{i}\sin\theta\cos\varphi + \mathbf{j}\sin\theta\sin\varphi + \mathbf{k}\cos\theta$$

Calculated D and E values for the assumed geometry and nuclear distance of 2.8Å are -0.3 and 0.01 cm^{-1}, respectively. The calculated isotropic J^{dip} value is ~ +10 cm^{-1}. The principal Z axis of the $\mathbf{D}_{\mathbf{AB}}{}^{\mathrm{dip}}$ tensor is nearly along the A-B direction. The considerable departure from the axial symmetry arises from the non-axial anisotropy of the present system which originates in the O1 atom.

The above model suggests that the observed ZFS parameters can be interpreted by the magnetic dipolar contribution between the two unpaired electrons localized on the copper(II) ions. In the framework of the above calculation, if J^{dip} dominates the spin alignment the singlet ground state is anticipated. In the present system, however, there are other competing mechanisms, particularly 90° superexchange interaction via the 2p orbital of the O1 oxygen atom between the two singly occupied 3d orbitals. The overlap of the 3d orbital with the 2p orbital is governed by the geometry of the bridge.[7-10] If the Cu1-O1-Cu1* angle is 90°, the overlap can be zero, but a variation in the angle can restore a non-zero overlap. In the case of the angle 180°, the "complete" overlap occurs, leading to the singlet ground state for dinuclear copper complexes. In the intradinuclear copper(II) complex **2'**, a disjoint bipyramidal structure is expected, but the molecular structure at the copper binding site is still strongly reinforced by the saturated azamacrocyclic ligand. In both the present dinuclear complexes **2**and **2'**, the molecular structural constraint by the reinforcement crucially gives rise to the contribution from the 90° superexchange interaction. Because of the rather remote distance R(Cu-O1) the contribution can compete with J^{dip}.

CONCLUSION

We have synthesized structurally reinforced chiral B_2-18-membered hezaazamacrocyclic amine based dinuclear copper(II) complexes **2** and **2'** for the purposes of studying the size-match selectivity of metal ions and the spin alignment of the intradinuclear copper(II) systems in terms of molecular structure-magnetism relationship. Because of the intradinuclear systems realized by the reinforcement, a subtle change in the molecular geometry gives rise to a prominent change in ESR fine structure. The competitive mechanisms to control the spin alignment have been discussed in terms of the magnetic dipolar interaction and superexchange interaction. The observed ZFS parameters for **2'** are interpreted by the dominant magnetic dipolar interaction model with the **g** anisotropy taken into account.

To our knowledge, documented dinuclear complexes of 18-membered azamacrocyclic amine ligands have been rare. From the powder-pattern ESR measurements of the complexes **2** and **2'** it has turned out that the structural reinforcement by the saturated polyazamacrocycle is efficient to exert a "genuine" size-match selectivity for intradinuclear metal ions.

In view of the electronic spin structure of the dinuclear complexes at hand, the exchange interaction between the copper pair can presumably be modulated in accordance with the geometry of the oxygen bridge. Thus, it is concluded that the structurally reinforced polyazamacrocyclic ligands give a useful model not only for controlling the propensity of the polyazacycle for binding to multiple metal ions in folded (cis) molecular conformations but also for tuning the molecular structure vs. magnetism relationship.

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