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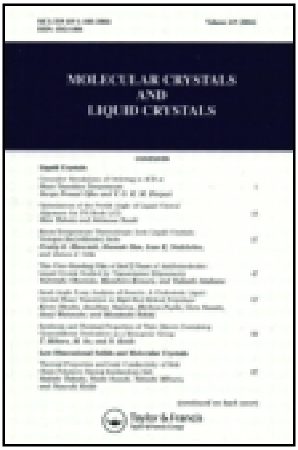

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Structurally Reinforced Chiral Macrocyclic Polyamine Based Dinuclear Copper (II) Complexes as Studied by CW and FT Pulsed ESR and Squid Measurements

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STRUCTURALLY REINFORCED CHIRAL MACROCYCLIC POLYAMINE BASED DINUCLEAR COPPER (II) COMPLEXES AS STUDIED BY CW AND FT PULSED ESR AND SQUID MEASUREMENTS

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Abstract We have attempted 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-mach selectivity of metal ions. From the viewpoint of molecular based magnetism-structure relationship, these two dinuclear complexes have manifested a prominent difference in the electronic structure, although only apparent structural difference is subtle. In the dinuclear complex **2'**, the fifth ligand is missing, forming slanting bi-squares with a common oxygen atom of hydroxide ion. CW ESR measurements of **2** and **2'** in polycrystalline solids have shown that a triplet fine-structure spectrum with a large zero-field splitting (ZFS) value features in **2'** and an exchange coupled copper(II) pair spectrum does in **2**, respectively. These findings have been expounded in connection with the structural difference in the macrocyclic rugbyball-shaped cavity of the ligand. The ground-state spin multiplicity for the copper dinuclear complexes has been rationalized in terms of a molecular orbital picture of 90 degree superexchange interaction via the bridging oxygen linker.

INTRODUCTION

Structurally reinforced saturated polyazamacrocyclic molecules have attracted considerable interest, since the bridging of adjacent secondary amino groups in the macrocycle as a ligand gives 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.

For the purposes of studying the size-match selectivity of metal ions, an attempt

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has been made to synthesize structurally reinforced chiral B_2-18-membered hexaazamacrocyclic amine based dinuclear copper(II) complexes **2** and **2'**. X-ray diffraction analyses[1] have shown that the dinuclear copper(II) complex **2** is joint square bipyramidal with a single common ridgeline Cl1-O1 and copper(II) lies nearly in each square plane, where Cl1 is a single axial ligand. The macrocyclic cavity is rugbyball-shaped.[1] In the dinulear copper(II) 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. Only the ORTEP view of the metal-binding site of **2** is shown in Figure 1.

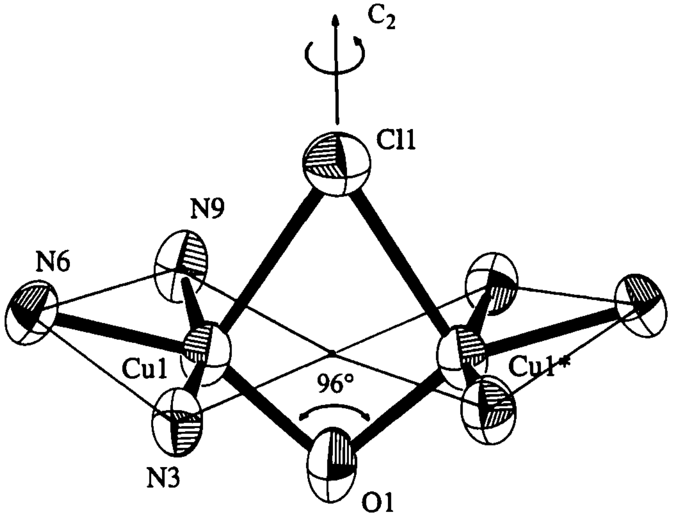

FIGURE 1 ORTEP view of the metal-binding site of the dinuclear copper(II) complex **2**.

MOLECULAR STRUCTURE OF JOINT BIPYRAMIDS 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 R(Cu-O1)=1.91Å. The distance between Cu1(or Cu1*) and Cl1 is 2.65Å, showing that they are remote, compared with R(Cu-N). The dihedral angel between

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the planes, N3N6N9 and N3*N6*N9* is approximately 150°. The angle between N6Cu1 and Cu1*N6* is 96°. The C_2 symmetry axis corresponds to the line Cl1-O1 as shown in Figure 1.

EXPERIMENTAL

The syntheses of **2** and **2'** will be published elsewhere.[2] The X-ray diffraction analysis of **2** and the details of the molecular structure and the molecular packing will be described elsewhere.[1] ESR measurements have been made with a Bruker ESP 300 spectrometer (X-band) equipped with an Oxford helium-gas flow variable temperature controller ESR910.

RESULTS AND DISCUSSION

Figure 2 shows a powder-pattern CW-ESR spectrum of **2** in polycrystalline solid observed at room temperature. The spectrum is characteristic of an exchange-coupled pair of copper(II) ions, revealing that the copper hyperfine structure is smeared out and

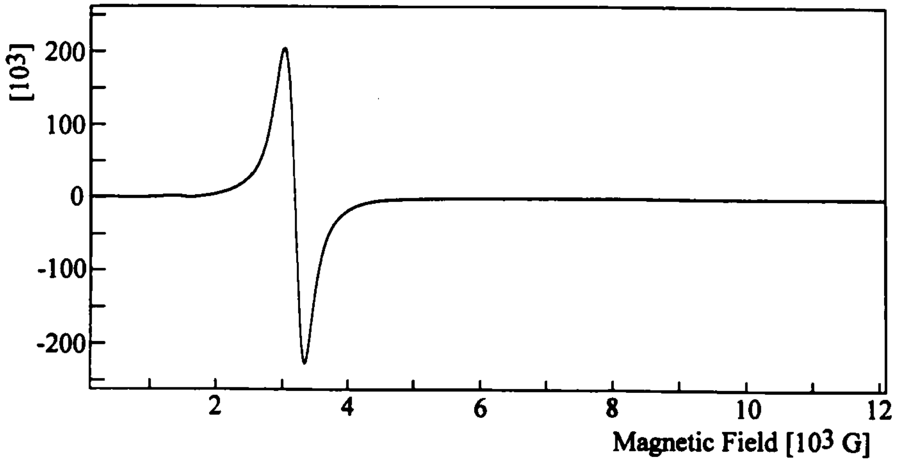

FIGURE 2 Power-pattern ESR spectrum of **2** in polycrystalline solid observed at room temperature. The vertical axis is in arbitrary units.

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only a residual g-anisotropy remains with a Lorentzian lineshape. With decreasing temperature down to 3K, the signal intensity increased without lineshape change observed, suggesting that the ground state of **2** is triplet. The single-crystal ESR spectra observed at room temperature have exhibited the residual g-anisotropy. Magnetic susceptibility measurements with a SQUID magnetometer are under way to characterize the bulk magnetic property of **2**.

On the other hand, typical powder-pattern fine-structure spectra have been observed from the copper(II) dinuclear complex **2'** in the wide range of 300 to 2.8 K, as shown in Figure 3. The spectrum in Figure 3 is characteristic of the triplet state with a large zero-field splitting (ZFS) parameter D from random orientation. The hyperfine structure due to copper(II) has been smeared out. In order to derive precise spin Hamiltonian parameters from the exchange-coupled triplet state from random orientation, lineshape simulation with exchange contribution taken into account is in progress. Also, theoretical calculation of the ZFS tensor for the exchange coupled copper pair is under way, assuming that the magnetic dipolar interaction dominates and the molecular structural parameters are similar to those of **2** in the copper(II) binding site.

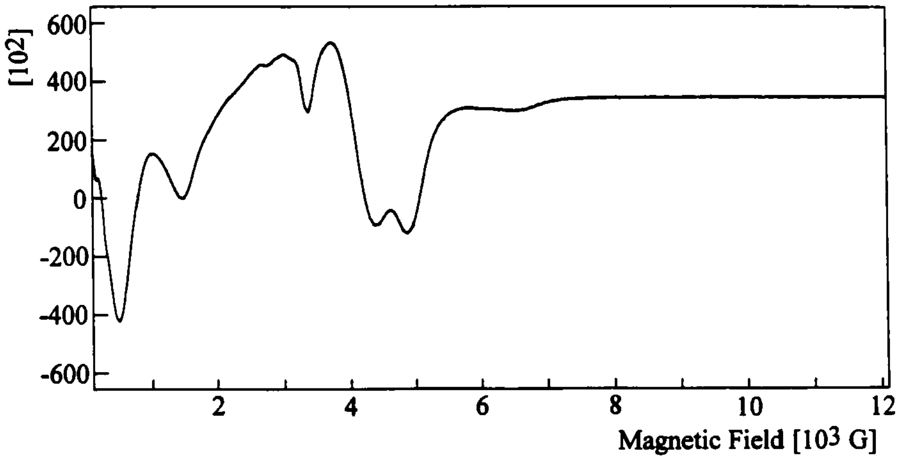

FIGURE 3 Powder-pattern ESR spectrum of **2'** (Cl1 missing) in polycrystalline solid observed at 2.8K. The vertical axis is in arbitrary units.

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In the dinuclear copper complex **2'**, a disjoint bipiramidal structure is expected, but the molecular structure in the copper binding site is still strongly reinforced by the saturated azamacrocyclic ligand. Compared with **2**, the copper dinuclear complex **2'** is categorized as strong exchange coupling. The ground-state triplet can be rationalized by considering how exchange interaction operates between the two single occupied 3d orbitals ($|3d: x^2 - y^2>$) via the 2p orbital of one oxygen bridge.[3,4] The overlap of the $|3d: x^2 - y^2>$ orbital with the 2p orbital is determined by the geometry of the bridge. 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, resulting in the singlet ground state for the dinuclear copper complex. In the intradinuclear copper complexes **2** and **2'** under study, the molecular structural constraint by the reinforcement crucially gives rise to the 90° overlap. A difference appearing in the observed ESR spectra, i.e., strong exchange for **2'** and intermediate or weak one for **2**, probably arises from a slight difference in the geometry of the oxygen bridge.[3-6]

CONCLUSION

We have synthesized structurally reinforced chiral B_2-18-membered hexaaza-macrocyclic amine based dinuclear copper(II) complexes **2** and **2'** for the purposes of studying the size-match selectivity of metal ions. To our knowledge, documented dinuclear complexes of 18-membered azamacrocyclic amine ligands have been rare. From the powder-pattern ESR measurements of **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 copper(II) complexes, the exchange interaction between the copper(II) pair can be presumably 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 magnetism vs. structure relationship. A complete characterization of the molecular structure and magnetic property of **2** and **2'** is under way.

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