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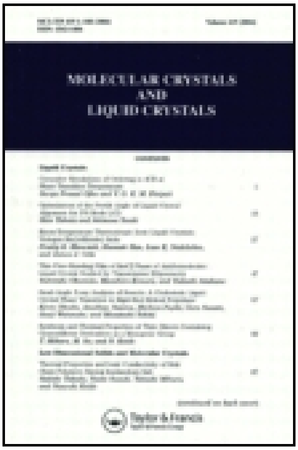

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Structurally Reinforced Chiral Macrocyclic Polyamine Copper (II) Complexes as Studied by ESR and Squid Measurements

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STRUCTURALLY REINFORCED CHIRAL MACROCYCLIC POLYAMINE COPPER (II) COMPLEXES AS STUDIED BY ESR AND SQUID MEASUREMENTS

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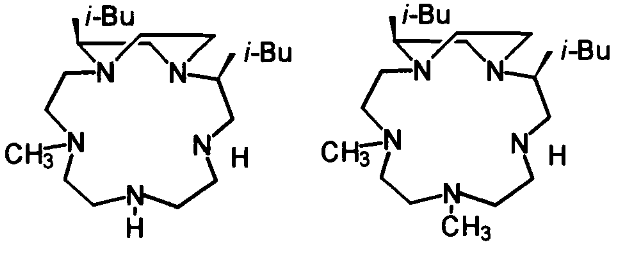
Abstract We have synthesized structurally reinforced chiral pentaaza-fifteen-membered polyamines **1** and **2** with a dibridge for the purposes of studying the size-match selectivity of the macrocyclic cavity. Particularly, an attempt has been made to synthesize copper(II) complexes of **1** and **2** to characterize the size-match selectivity of the polyamines in term of microscopic details of the metal-ion binding site. For this purpose the use of ESR spectroscopy has been invoked before X-ray structural analyses of the complexes are carried out. Powder-pattern ESR spectra of the copper(II) complex of **1** in crystalline solid have revealed a temperature dependence of the copper hyperfine structure. This finding suggests that a vibronic effect features in the hyperfine spectra, showing that the pentaaza-macrocycle under study accommodates copper(II) ion and the macrocycle is flexible to exert "genuine" size-match selectivity.

INTRODUCTION

Structurally reinforced saturated azamacrocyclic molecules have attracted considerable interest,[1-3] since the bridging of adjacent secondary/tertiary amino groups in the macrocycle as a ligand gives a facile method for controlling the propensity of the azacycle for binding to a metal ion in a folded molecular conformation.

We have synthesized structurally reinforced chiral pentaaza-fifteen-membered polyamines **1** and **2** with a bridge, as shown in Figure 1, for the purposes of studying the size-match selectivity of the macrocyclic cavity. The synthetic procedure is described only briefly in this paper.[4] An attempt has been made to synthesize copper(II) complexes of 1 and 2 to characterize the size-match selectivity of the polyamine cages in term of microscopic details of the metal-ion binding site. For this purpose we have measured ESR spectra of the copper(II) complexes in polycrystalline solids before X-ray structural analyses of the complexes are carried out.



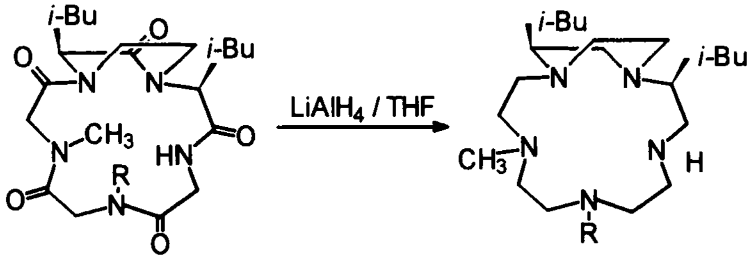
1 **2**

FIGURE 1 Structurally reinforced chiral pentaaza-fifteen membered polyamines under study.

EXPERIMENTAL

Syntheses of structurally reinforced chiral macrocyclic polyamines 1 and 2

The synthetic routes will be published elsewhere[4] and are given only briefly in Figure 2.



1 (R=H), **2** (R=CH$_3$)

FIGURE 2 Synthetic routes of structurally reinforced chiral pentaaza-fifteen-membered polyamines 1 and 2

Syntheses of the copper(II) complexes of 1 and 2

The syntheses of the copper(II) complexes of 1 and 2 have been carried out as follows:

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Methanol solutions of **1** and **2** were stirred with $Cu(ClO_4)_2 \cdot 6H_2O$ for several hours and evaporated to give powder in violet color. The copper(II) complexes were recrystallized from hot water.

ESR measurements

The ESR spectra of the copper(II) complexes of **1** and **2** in polycrystalline solids have been measured with a Bruker ESP 300 ESR spectrometer operating at X-band equipped with an Oxford helium-gas flow variable temperature controller ESR910 cryostat. The temperature dependence of the ESR spectra has also been measured with a JOEL FE-2XG(X-band) ESR spectrometer in the double field modulation mode with 80Hz and 100kHz, equipped with a nitrogen-gas flow variable temperature controller DVT-2.

RESULTS AND DISCUSSION

We have observed the powder-pattern ESR spectra from the copper(II) complex of **1** in a wide range of temperature. The spectra have revealed poorly resolved hyperfine structures due to copper(II) and axial g-anisotropy in spite of magnetically concentrated samples; This suggests that the sizable and folded molecular conformation of the macrocyclic cavity prevent the magnetic copper(II) ions embraced in the macrocyclic polyamines from being close enough to undergo exchange interaction.

The powder-pattern ESR spectrum from the copper(II) complex of **1**, shown in Figure 3, is characteristic of axial g-anisotropy, indicating that the copper is accommodated in the environment of a tetragonally distorted octahedral symmetry. The observed g-anisotropy strongly suggests that the copper(II) ion sits in an approximately square planar ligand field surrounded by four nitrogen atoms. Since the macrocyclic pentaaza polyamine **1** is structurally reinforced by the dibridging of adjacent amino groups in the macrocycle, the nitrogen atom located furthest from the dibridged two nitrogen ones is not capable of participating in the square-plane environment. Instead, the furthest nitrogen is in a position of an axial ligand together with a single ClO_4^- ion. Whether the furthest nitrogen weakly binds on the same side as the ClO_4^- ion does is

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still an open question. Nevertheless, the binding on the same side is probable, considering the crowdedness of the other side.

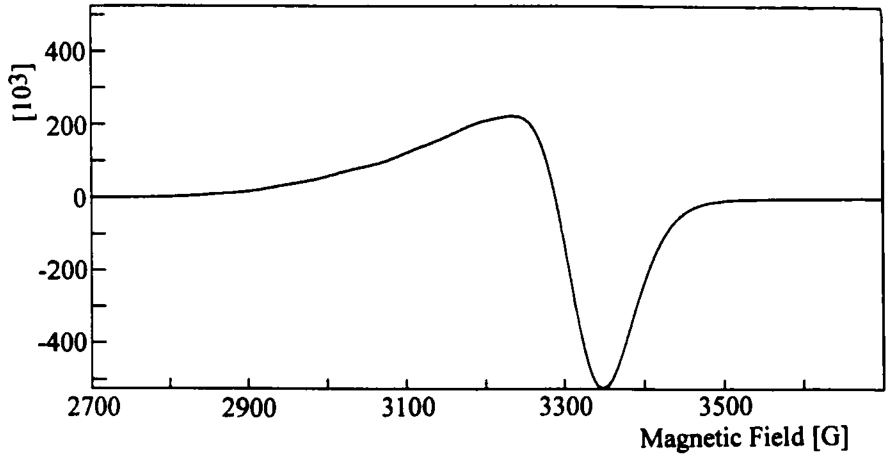

FIGURE 3 Powder-pattern ESR spectrum of the copper(II) complex of **1** observed at room temperature in the polycrystalline solid. The vertical axis is in arbitrary units.

The temperature dependence of the copper hyperfine structure observed in the range down to 4 K strongly suggests that the observed phenomenon is due to a vibronic effect (vibrationally modulated hyperfine structure). The magnitude of the copper hyperfine splitting decreased with decreasing temperature, indicating that a change in the tetragonal distortion took place. The change reflects the flexibility of the macrocyclic pentaaza polyamine **1** as a ligand in terms of microscopic details. In order to identify vibrational modes responsible for the observed phenomenon, more precise determination of the copper hyperfine structure tensor is required as well as the observation of superhyperfine structure due to the binding nitrogen nuclei.

On the other hand, the copper(II) complex of **2** has not revealed any appreciable temperature dependence of the copper hyperfine structure in the powder-pattern ESR spectra in the range of room temperature to 4 K. The copper hyperfine splitting has been evaluated to be as small as one corresponding to the ESR spectrum of the copper(II) complex of 1 observed below 77K. The findings indicate that the macrocyclic pentaaza polyamine **2** as a ligand is not so flexible as **1**, showing that chemical modification of structurally reinforced macroclyclic polyamines can be useful to exert "genuine" size-match selectivity of metal-ions. Also, the macrocyclic pentaaza polyamines under study can be suitable models for studying vibronic effects occurring in low-symmetric fields of sizable molecular frames with biological implications.

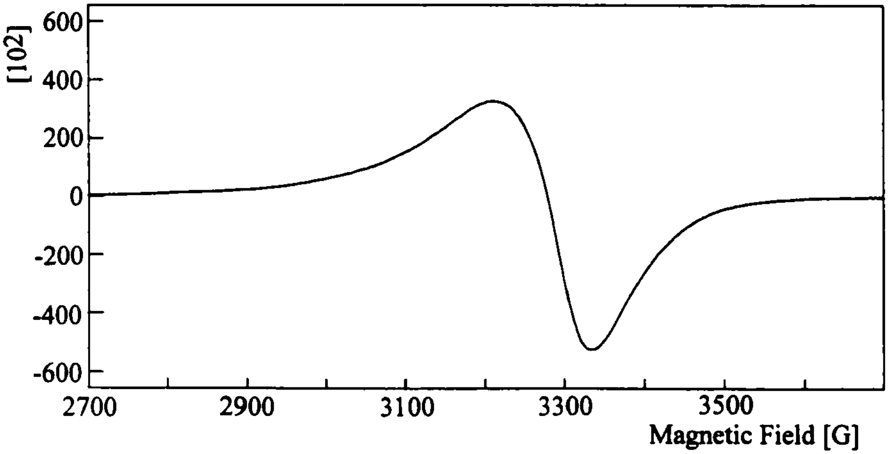

FIGURE 4 Powder-pattern ESR spectrum of the copper(II) complex of **2** observed at 7K in the polycrystalline solid. The vertical axis is in arbitrary units.

CONCLUSION

Structurally reinforced saturated chiral pentaaza-fifteen-membered polyamines and their copper(II) complexes have been synthesized in order to study the size-match selectivity of their macrocyclic cavity. For this purpose the use of ESR spectroscopy has been invoked before X-ray diffraction analyses of their single crystal are carried out. The powder-pattern ESR spectra from the copper(II) complexes of **1** and **2** in polycrystalline solids have shown that the pentaaza macrocycles under study accommodate copper(II) ion in the tetragonally distorted octahedral symmetry of the ligand field. It has turned out from the temperature dependence of the copper hyperfine structure of the complex of **1** that the macrocycle is flexible to exert "genuine" size-match selectivity of metal ions.

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In order to identify the vibrational mode responsible for the temperature dependence and to study the electronic and molecular structure of the metal binding site, ESR spectroscopy of the magnetically diluted copper(II) complexes is under way as well as magnetic susceptibility measurements with a SQUID magnetometer. Also, molecular conformational studies on the copper(II) complexes of **1** and **2** in fluid solution are in progress by the use of CW and FT-pulsed ESR spectroscopy.

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