学位論文要旨

Synthesis of $Cu(hfac)_2$ Complexes with 3-Pyridyl-Substituted Nitroxide Radicals and Study Their Physical Properties

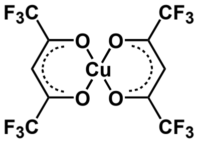
(3-ピリジル置換ニトロキシドラジカルを有する$Cu(hfac)_2$錯体の合成及び物性評価)

Tatiana Sherstobitova

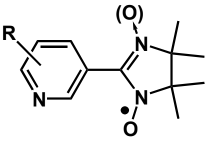
Introduction

Copper(II) complexes with nitroxide radicals have recently attracted particular attention. Their magnetic behavior strongly correlates with the geometry of the coordination Cu^{2+} sphere, which is substantially affected by the molecular structure of nitroxide ligand. The equatorial coordination of the nitroxyl group (NO group) results in the strong antiferromagnetic Cu^{2+}-radical exchange coupling ($J \ll 0$), while the axial binding leads to ferromagnetic exchange interactions ($J > 0$). In some cases, the energy gap between equatorial and axial coordination is very weak that allows switching magnetic exchange interactions by change of temperature, pressure or light irradiation.

Only a few numbers of the Cu(II) complexes with nitroxides exhibit structural-magnetic anomalies under external stimuli. Even a minor modification of a ligand leads to significant change in molecular and crystal structures of the resulting complexes. That strongly affects the parameters of magnetic transitions as well as can be resulted in the assembly of phases that cannot exhibit any structural-magnetic anomalies. $Cu(hfac)_2$ complexes with various derivatives of 3-pyridyl-substituted nitronyl and imino nitroxides (NN/ImN-3Py) are of special interest due to their diversity of molecular species and magnetic properties. Introduction of Me group into the 4th position of the pyridine ring for NN-3Py ligand has led to the formation of $Cu(hfac)_2$ complexes with different structures and magnetic behavior. The aim of performed research was the study of the effect of substituents located in the 2nd, 5th or 6th positions of the pyridine heterocycle on the coordination ability of NN/ImN-3Py$^{\mathbf{R}}$ ligands and structure and magnetic behavior of the resulting $Cu(hfac)_2$ complexes. Me and Br groups were chosen as substituents since both of them have the same spatial size, but different electronic properties. Important tasks in the study of the physical properties of Cu(II)-nitroxide complexes included the investigation of the effect of pressure on the magnetic behavior of the selected complexes and the development of a method for measuring the temperature dependence of the dielectric constant for materials undergoing magnetic anomalies.



$Cu(hfac)_2$



NN/ImN-3Py^R
R = Me, Br

Results and Discussion

1. $Cu(hfac)_2$ complexes with Me- and Br-Substituted 3-Pyridyl Nitronyl Nitroxides

Reaction of $Cu(hfac)_2$ with NN-3Py^R (R = Me, Br) led to the assembly for the diverse set of coordination complexes: mononuclear [$Cu(hfac)_2$NN-3Py$^{2\text{-Me}}$], binuclear [$\{Cu(hfac)_2\}_2(H_2O)$NN-3Py$^{2\text{-Me}}$], trinuclear [$\{Cu(hfac)_2\}_3$(NN-3Py$^{6\text{-Br}}$)$_2$], pentanuclear [$\{Cu(hfac)_2\}_5$(NN-3Py$^{2\text{-Me}}$)$_2$] and [$\{Cu(hfac)_2\}_5$(NN-3Py$^{2\text{-Me}}$)$_4$], cocrystals [$Cu(hfac)_2$(NN-3Py$^{2\text{-Br}}$)$_2$]·[$Cu(hfac)_2(H_2O)_2$] and [$Cu(hfac)_2$(NN-3Py$^{2\text{-Br}}$)$_2$]·2[$Cu(hfac)_2H_2O$], 1D polymers [$Cu(hfac)_2$NN-3Py$^{2\text{-Br}}$]$_n$ and [$Cu(hfac)_2$NN-3Py$^{6\text{-Br}}$]$_n$, and cyclic dimers [$Cu(hfac)_2$NN-3Py$^{5\text{-Me}}$]$_2$, [$Cu(hfac)_2$NN-3Py$^{5\text{-Br}}$]$_2$, and [$Cu(hfac)_2$NN-3Py$^{6\text{-Me}}$]$_2$. Molecular structures of obtained complexes are strongly affected by substituent type and its location in the pyridine heterocycle. Occupation of the 2nd position of the pyridine ring increases the steric hindrance for both imine (N_{Py}) and nitroxide coordination sites of NN-3Py$^{\mathbf{2\text{-}R}}$ (R = Me, Br) that is favorable for the formation of various conformers and precipitation of complexes with different molecular structures. Unique pentanuclear [$\{Cu(hfac)_2\}_5$(NN-3Py$^{2\text{-Me}}$)$_2$] and [$\{Cu(hfac)_2\}_5$(NN-3Py$^{2\text{-Me}}$)$_4$] complexes have not prior analogs and are valuable model objects for investigation of a mechanism for the formation of various coordination polymers. The arrangement of long Cu-O_{NO} bonds due to the weakening nitroxide donor site in complexes based on NN-3Py$^{\mathbf{2\text{-}R}}$ (R = Me, Br) ligands results in the ferromagnetic exchange interactions in three-spin coupled {>N-•O-Cu^{2+}-O•-N<} clusters. Complexes, where substituents do not considerably affect the coordination ability of ligands (NN-3Py$^{5\text{-Me}}$, NN-3Py$^{5\text{-Br}}$, NN-3Py$^{6\text{-Me}}$), exhibit strong antiferromagnetic exchange interactions between spins of Cu^{2+} ion and nitroxide.

2. Cu(hfac)$_2$ complexes with Me- and Br-Substituted 3-Pyridyl Imino Nitroxides

Introduction of Me and Br groups into the 2nd, 5th or 6th positions of the pyridine ring for ImN-3Py resulted in obtaining of eight Cu(hfac)$_2$ complexes: mononuclear [Cu(hfac)$_2$ImN-3Py$^{\mathbf{2\text{-}Br}}$], trinuclear I-[{Cu(hfac)$_2$}$_3$(ImN-3Py$^{\mathbf{2\text{-}Me}}$)$_2$], II-[{Cu(hfac)$_2$}$_3$(ImN-3Py$^{\mathbf{2\text{-}Me}}$)$_2$], [{Cu(hfac)$_2$}$_3$(ImN-3Py$^{\mathbf{2\text{-}Br}}$)$_2$], [{Cu(hfac)$_2$}$_3$(ImN-3Py$^{\mathbf{6\text{-}Me}}$)$_2$], and [{Cu(hfac)$_2$}$_3$(ImN-3Py$^{\mathbf{6\text{-}Br}}$)$_2$], and tetranuclear cyclic dimers [{Cu(hfac)$_2$}$_2$(ImN-3Py$^{\mathbf{5\text{-}Me}}$)]$_2$, [{Cu(hfac)$_2$}$_2$(ImN-3-Py$^{\mathbf{5\text{-}Br}}$)]$_2$. Location of substituents in the least sterically hindered 5th position results in obtaining of tetranuclear [{Cu(hfac)$_2$}$_4$(ImN-3Py$^{\mathbf{5\text{-}R}}$)$_2$] complexes, where all three coordination sites of ImN-3Py$^{\mathbf{5\text{-}R}}$ are coordinated by Cu^{2+}. Steric hindrance for the 2nd and 6th positions of the pyridine heterocycle essentially reduces donor ability for the N$_{Py}$ site and the NO group (up to the absence of coordination). Various crystal packing of trinuclear [{Cu(hfac)$_2$}$_3$(ImN-3Py$^{\mathbf{R}}$)$_2$] (R = Me, Br) complexes causes the diversity of their magnetic behavior due to different intermolecular magnetic exchange interactions. Occupation of the 2nd position by Me group or Br atom favorable both to the formation of several polymorphs and to the realization of phase transitions in solids associated with switching of intermolecular magnetic exchange interactions (Figure 1). It was shown that application of pressure ~0.56 GPa for II-[{Cu(hfac)$_2$}$_3$(ImN-3Py$^{\mathbf{2\text{-}Me}}$)$_2$] results in stabilization of strongly-coupled state between spins of nitroxide ligands in room temperature region (Figure 1a).

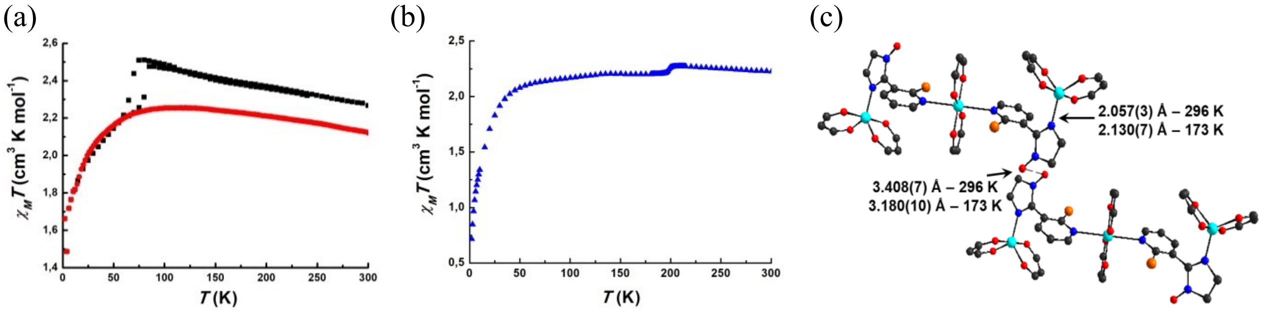


Figure 1. Temperature dependences of $\chi_M T$ for (a) II-[{Cu(hfac)$_2$}$_3$(ImN-3Py$^{\mathbf{2\text{-}Me}}$)$_2$] (■) – 10^{-4} GPa, (●) – 0.56 GPa and (b) [{Cu(hfac)$_2$}$_3$(ImN-3Py$^{\mathbf{2\text{-}Br}}$)$_2$] (▲) and (c) structure of [{Cu(hfac)$_2$}$_3$(ImN-3Py$^{\mathbf{2\text{-}Br}}$)$_2$].

3. Thermal Variation of Permittivity for Cu(hfac)$_2$ Complexes with 3-Pyridyl Nitronyl Nitroxide Ligand

Temperature variable dielectric measurements of the powdered polycrystalline pelleted sample for the [{Cu(hfac)$_2$}$_4$(NN-3Py)$_2$] tetranuclear dimer complex (Figure 2a) reviled the gradual change of permittivity in the temperature region of 40-120 K (Figure 2b). That is in agreement with the magnetic transition from weakly ferromagnetic to strongly antiferromagnetic coupled states for [{Cu(hfac)$_2$}$_4$(NN-3Py)$_2$].

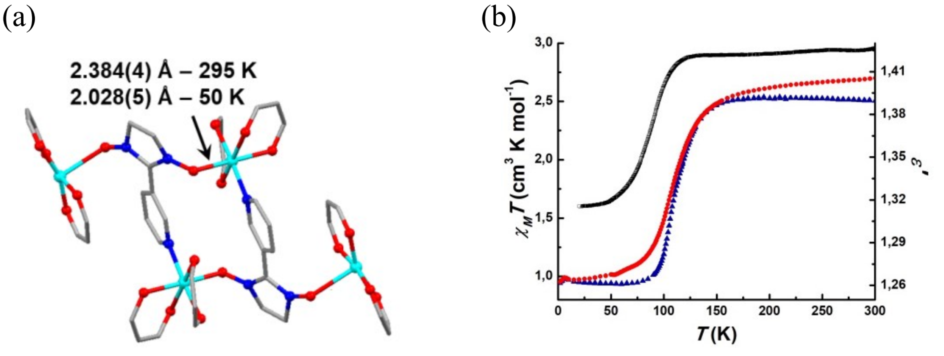
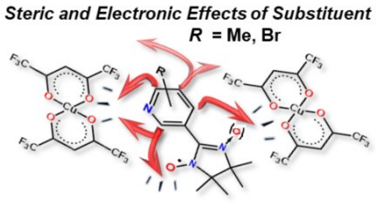


Figure 2. (a) Structure and (b) temperature dependences of permittivity at 316 kHz (■) and $\chi_M T$ for ▲ – solid and ● – pelleted samples for [{Cu(hfac)$_2$}$_4$(NN-3Py)$_2$].

Conclusion



Changing of electronic and steric properties for substituents allows tuning the donor ability of coordination sites for the Me- and Br-substituted NN/ImN-3Py$^{\mathbf{R}}$ ligands. This can serve as a powerful tool for the assembly of Cu(II) complexes with diverse molecular and crystal structures and different magnetic behavior. The studied pressure effect on magnetic properties of obtained complexes and investigation of peculiarities for thermally induced switching of dielectric constant can give valuable information about the nature of driving force and mechanism of phase transitions in Cu(II)-nitroxide complexes that can be useful for creation of new types of electronic devices for pressure/temperature detection and for data storage.