An HFEPR Study of a Nickel(II)-doped Dinuclear Zinc(II) Complex

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Introduction

The magnetic properties of metallic clusters are of continuous interest, as there are still many open questions in this regard. Because polynuclear systems are difficult to treat theoretically, we have concentrated on dinuclear species, and in particular on the origin of their magnetic anisotropy. Recently, we found a homo-dinuclear cobalt(II) complex that showed a strong magnetic anisotropy [1,2]. We also obtained an isomorphous nickel(II) complex [3], and we successfully determined the spin Hamiltonian parameters, in particular the zero-field splitting (ZFS), for its thermally-excited triplet excited state, by high-frequency and -field EPR (HFEPR) [4]. In order to understand the relationship between the ZFS parameters of the monomeric nickel(II) ion and the dinuclear triplet state, we prepared a nickel(II)-doped dinuclear zinc(II) complex and submitted it to HFEPR experiments.

Experimental

The nickel(II)-doped dinuclear zinc(II) complex $[Zn_2(sym\text{-hmp})_2](BPh_4)_2$ was synthesized using 2,6-bis[(2-hydroxyethyl)methylaminomethyl]-4-methyl-phenol [H(sym-hmp)] by mixing $NiCl_2{\cdot}6H_2O$ in the concentration of 5% into the procedure of preparing the dinuclear zinc(II) complex. In HFEPR experiments, the EMR facility at NHMFL was used, including its 15/17 T superconducting magnet.

Results and Discussion

Crystal structure of $[Zn_2(sym\text{-hmp})_2](BPh_4)_2$ was determined, and it was found to be very similar to its nickel derivative $[Ni_2(sym\text{-hmp})_2](BPh_4)_2$. Therefore, the environment of the nickel ion in the nickel(II)-doped dinuclear zinc(II) complex is also thought to be similar to that in the dinuclear nickel(II) complex. Figure 1 shows the field/frequency map of EPR resonances observed in Ni-doped $[Zn_2(sym\text{-hmp})_2](BPh_4)_2$. From this map, the ZFS parameters for the ground triplet state of the Ni(II) complex were obtained as $|D|$ = 10.0 cm^{-1}, E = 3.2 cm^{-1}, and g(iso) = 2.2. Single-frequency spectra (not shown) proved the positive sign for D which is consistent with the expected coordination geometry around the nickel(II) ion in the crystal since the coordination of the alcoholic oxygen atoms is weaker than that of the other ligands. Moreover, the observed magnitude of D is excellent agreement with the prediction based on the ZFS of the thermally-excited triplet state of the dinuclear $[Ni_2(sym\text{-hmp})_2](BPh_4)_2$ complex reported previously [4].

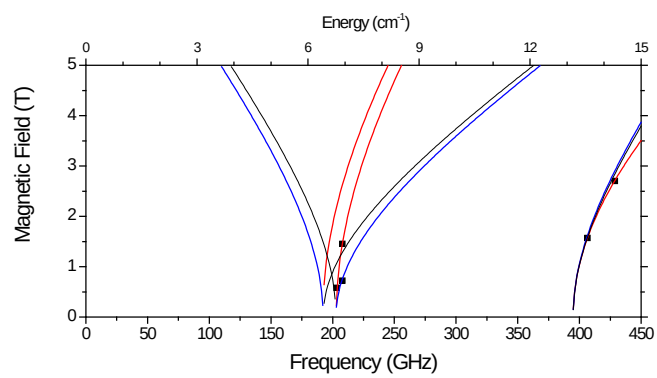

Figure 1. Field vs. frequency map of resonances observed in Ni-doped $[Zn_2(sym\text{-hmp})_2](BPh_4)_2$ at 5 K. Squares are experimental points; lines were simulated using spin Hamiltonian parameters as in text.

Conclusions

The ZFS parameters were estimated for the nickel(II)-doped dinuclear zinc(II) complex $[Zn_2(sym\text{-hmp})_2](BPh_4)_2$, and the observed positive D value is consistent with the expected coordination geometry around the nickel(II) ion.

Acknowledgements

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References

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