# EPR Studies of Pentacoordinate Mononuclear Cobalt Single-Molecule Magnets

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## Introduction

Two new mononuclear Co(II) complexes that have bis(imino)pyridine pincer ligands in conjuction with two isothiocyanate ligands have recently been synthesized [1]: **1** [{ArNCMe}$_2$(NPh)]Co(NCS)$_2$ and **2** [{ArNCPh}$_2$(NPh)]Co(NCS)$_2$. These two compounds have a distorted square-pyramidal geometry with the Co(II) centers lying above the basal plane. In **1,** the cobalt sits above the basal $N_4$ mean plane by 0.39 Å, meanwhile **2** has a more pronounced distortion with the metal center lying out of the basal $N_4$ plane by 0.52 Å. The elevation of the Co centers out of the square pyramidal basal plane, as is observed for compounds **1** and **2,** leads to significant spin-orbit coupling for the $d^7$ Co(II) ions and consequently to slow relaxation of the magnetization that is characteristic of Single-Molecule Magnet (SMM) behavior.

## Experimental

Constrained-powder EPR data were collected at 2.2 K in the EMR facility using a transmission probe and a 17 T superconducting magnet. High-frequency microwaves (50-430 GHz) were generated by a phase-locked Virginia Diodes solid-state source operating at 13±1 GHz, followed by a chain of multipliers.

## Results and Discussion

EPR measurements are key to providing an understanding of the observed magnetic features and help direct efforts in designing complexes with improved magnetic properties. We report preliminary powder EPR measurements that provide a quick and direct means to ascertain the *g*-anisotropy associated with the effective *S* = 1/2 ground state Kramers doublet. **Figure 1** shows multi-frequency EPR data for the two complexes. Both have significant anisotropies, evidenced by the considerable spread in the components of the effective *g*-tensors. Compound **2** has more *g*-anisotropy (0.91 to 8.51) compared to compound **2 (**1.44 to 7.24). This might be related to the fact that **1** has the cobalt center further away from basal plane. Electronic structure calculations are in progress in order to attempt to rationalize the differences in anisotropy observed for the two compounds.

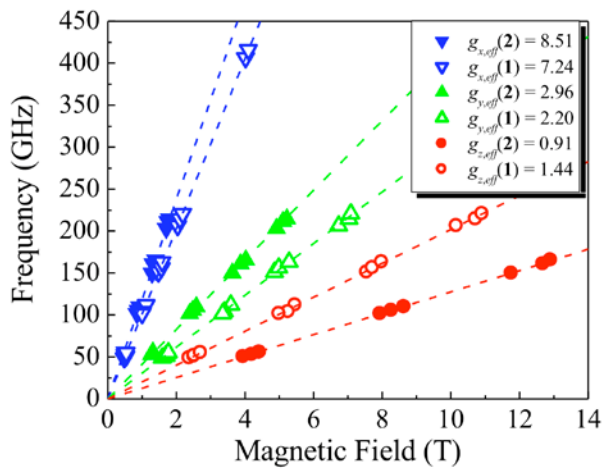


**Figure 1.** Multi-frequency powder EPR data for compounds **1** and **2** collected at 2.2 K**.**

## Conclusions

Powder EPR studies have been carried out on two new pentacoordinate mononuclear Co(II) complexes that reveal significant *g*-anisotropies associated with the effective *S* = 1/2 ground state Kramers doublets. Compound **2** has more *g*-anisotropy (0.91 to 8.51) compared to compound **1** (1.44 to 7.24). This might be related to the fact that **2** has the cobalt center further away from basal plane of the distorted square-pyramidal geometry.

## Acknowledgements

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## References

[1] Jurca, T., *et al.*, J. Am. Chem. Soc., **133**, 15814-15817 (2011).