# TUNABLE-FREQUENCY HIGH-FIELD EPR OF A SERIES OF COBALT(II) "SCORPIONATE" COMPLEXES AS MODELS FOR ZINC ENZYMES

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## Introduction

The trispyrazolylborate "scorpionate" ($Tp^{-}$) is a monoanionic, 3N-donor ligand that binds a wide variety of transition metal ions. Substituent groups on the pyrazole rings, designated as $Tp^{R,R'-}$, allow fine tuning of the electronic properties of the ligand. Four-coordinate scorpionate complexes of Co(II) ($3d^7$, $S = 3/2$) can serve as spectroscopically active models for many zinc proteins, wherein the spectroscopically "silent" Zn(II) is coordinated by three histidine imidazole nitrogens.[1]

## Experimental

The Mm and Sub-mm Wave Spectroscopy Facility and the 25-T "Keck" magnet were used to study polycrystalline samples of an extensive series of $Tp^{R,R'}CoL$ complexes, where R = 3- substituent, R' = 4-substituent, and L = $Cl^{-}$, $N_3^{-}$, $NCO^{-}$, $NCS^{-}$.

## Results and Discussion

Tunable high-frequency and-field EPR (HFEPR) provided definitive values of the spin Hamiltonian parameters for high-spin Co(II) in biologically relevant coordination environments as given in Table 1 below.

Table 1. Spin Hamiltonian parameters for the investigated $Tp^{R,R'}CoL$ complexes.

| Complex | $D$ ($cm^{-1}$) | $E$ ($cm^{-1}$) | $g_x$ | $g_y$ | $g_z$ |
|---|---|---|---|---|---|
| $Tp^{t\text{-}Bu}CoCl$ | +10.88(1) | +0.21(6) | 2.34(2) | 2.32(2) | 2.11(2) |
| $Tp^{t\text{-}Bu,Tn}CoCl$ | +12.72(4) | +0.78(2) | 2.36(1) | 2.20(1) | 2.25(1) |
| $Tp^{t\text{-}Bu,Me}CoCl$ | +11.52(2) | +0.141(1) | 2.35(1) | 2.35(1) | 2.24(1) |
| $Tp^{i\text{-}Pr,Br}CoCl$ [a] | +13.3 | +1.4 | 2.25 | 2.15 | 1.95 |
| $Tp^{t\text{-}Bu}CoN_3$ | +7.457(2) | +1.575(3) | 2.48(2) | 2.02(1) | 2.31(2) |
| $Tp^{t\text{-}Bu,Me}CoN_3$ | +6.32(2) | +0.48(4) | 2.70(2) | 2.46(2) | 2.18(2) |
| $Tp^{t\text{-}Bu}Co(NCO)$ | +5.98(2) | +0.169(23) | 2.29(2) | 2.43(2) | 2.16(1) |
| $Tp^{t\text{-}Bu,Me}Co(NCO)$ | +5.37(2) | +0.43(3) | 2.16(2) | 2.27(3) | 2.222(5) |
| $Tp^{t\text{-}Bu}Co(NCS)$ | +2.39(3) | +0.153(15) | 2.27(1) | 2.28(1) | 2.21(1) |
| $Tp^{t\text{-}Bu,Tn}Co(NCS)$ | +3.34(1) | +0.49(1) | 2.24(1) | 2.27(1) | 2.229(5) |
| $Tp^{t\text{-}Bu,Me}Co(NCS)$ | +2.69(1) | +0.15(1) | 2.16(1) | 2.18(1) | 2.223(5) |

[a] The data for $Tp^{i\text{-}Pr,Br}CoCl$ have not been yet properly fitted, hence we do not show error estimates.

## Conclusions

The accuracy of the spin Hamiltonian parameters obtained from the title technique is much higher than that from other methods, such as X-band EPR power saturation or MCD, as will be described in manuscript in progress.

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## References

[1] Trofimenko, S., *et al.* Inorg. Chem., **26**, 1507-1514 (1987).