TUNABLE-FREQUENCY HIGH FIELD EPR OF A SERIES OF COBALT(II) "SCORPIONATE" COMPLEXES

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Introduction

In the mid-1960's, S. Trofimenko, then at E. I. du Pont de Nemours & Co., first prepared trispyrazolylborates (Tp). These compounds have proven to be very effective and versatile ligands for a very wide variety of d and f block metal ions. Their mode of chelation has led to their being dubbed "scorpionate" ligands, as shown in Fig. 1.

Experimental

A series of complexes of general formula [Tp(R)(R')CoX], where X = Cl, NCS, NCO, N_3, and R = substituent on the 3 position of the pyrazole ring, R' = 4-substituent, were synthesized as described previously.[1] These were studied as microcrystalline powders using the Mm and Sub-mm Wave Spectroscopy Facility and the 25-T "Keck" magnet.

Results and Discussion

The results for a wide series of high-spin (S = 3/2) 4-coordinate Co(II) scorpionate complexes are summarized in Table 1. Parallel studies of electronic absorption spectra and x-ray crystallography are in progress.

Table 1. Spin Hamiltonian Parameters for [Tp(R)(R')CoX] Complexes Determined by HFEPR.

X =	NCS	NCO	N_3	Cl
Tp(*t*Bu) (R = *t*-butyl) (R' = H)	D = 2.6 cm^{-1} E = 0.2 cm^{-1} g = 2.2, 2.3, 2.25	D = 5.9 cm^{-1} E = 0.2 cm^{-1} g = 2.35, 2.35, 2.15	D = 7.8 cm^{-1} E = 1.0 cm^{-1} g = 2.15, 2.15, 2.15	D = 10.85 cm^{-1} E = 1.0 cm^{-1} g = 2.33, 2.3, 2.15
Tp(*t*Bu,Tn) (R = *t*-butyl) (R' = thienyl)	D = 3.46 cm^{-1} E = 0.51 cm^{-1} g = 2.25, 2.25, 2.2	D = 10.9 cm^{-1} E = 0.0 cm^{-1} g = 2.25, 2.25, 2.2	$D \approx$ 5 cm^{-1}	D = 12.7 cm^{-1} E = 0.5 cm^{-1} g = 2.25, 2.25, 2.3
Tp(*t*Bu,Me) (R = *t*-butyl) (R'= methyl)	D = 2.6 cm^{-1} E = 0.2 cm^{-1} g = 2.2, 2.2, 2.2	D = 5.2 cm^{-1} E = 0.45 cm^{-1} g = 2.3, 2.3, 2.2	D = 6.45 cm^{-1} E = 0.3 cm^{-1} g = 2.6, 2.6, 2.1	D = 11.5 cm^{-1} E = 0.0 cm^{-1} g = 2.35, 2.35, 2.25

Conclusions

HFEPR allows rapid and accurate determination of electronic parameters for high-spin Co(II) in a series of 4-coordinate scorpionate complexes. These data will allow correlation of metal ion electronic structure with organic substituents of ligands to allow tuning of desired properties for catalysis and as models for 4-coordinate Zn enzymes with tris histidine coordination.

Acknowledgements

We thank NHMFL and Roosevelt University.

References

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