Determination of the Zero-field Splitting in a Series of Tetracoordinate Cobalt(II) Complexes by Electron Paramagnetic Resonance

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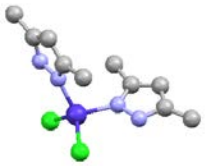
Introduction

Tuning the magnetic anisotropy, i.e. tailoring the axial zero-field splitting parameter *D* in transition metal complexes, is far from being routine. It represents one of the open questions addressed by experimental and theoretical chemists nowdays which can facilitate a rational synthesis of single molecule magnets. Some magnetostructural *D*-correlations have been outlined recently, applicable to hexacoordinate Ni(II) and Co(II) complexes [1, 2]. Their extension to other central atoms and other coordinations requires reliable data sets based upon a combined application of magnetometry and HFEPR to structurally fully characterize compounds of interest.

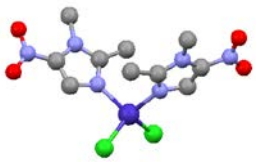
Experimental

Chemical synthesis yielded a set of tetracoordinate $[CoCl_2L_2]$ complexes containing various N-donor ligands (**Table 1**) which were structurally fully characterized by X-ray diffraction. The SQUID magnetic data (susceptibility and magnetization) were a basis for a conventional $S = 3/2$ spin Hamiltonian parameters fit, which bracketed *the D*-values. The same powder samples were subjected to HFEPR experiments using both the superconducting 15/17 T magnet of the EMR Facility, and the 25 T resistive "Keck" magnet of the DC Facility, in a wide range of frequencies (50 – 700 GHz). In addition to the *g*-factors and *D*-parameters, the *E*-values were also determined.

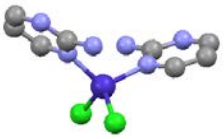
Table 1. Molecular structure of the $[CoCl_2L_2]$ complexes selected for SQUID and HFEPR studies. Preliminary SQUID-determined values for *D* [cm^{-1}] are in parentheses followed by the preliminary HFEPR parameters.



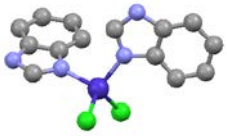
A dimethylpyrazole
(+42), large



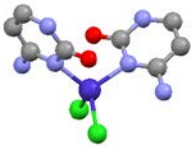
B nitrodimethylimidazole
(+11.4), +11.40



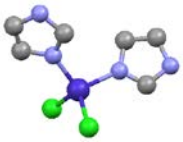
C aminopyrimidine
(+12.2), –8.02



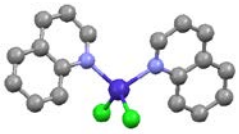
D benzimidazole
(–3.1), ±3.29



E cytosine
(–4.4) –4.31



F imidazole
(–7.8), –8.3



G quinoline
(+6.6), –5.95

Results and Discussion

The retrieved set of *D*-parameters via HFEPR experiments basically match the values preliminary determined upon analysis of susceptibility and magnetization data. However, in some cases the sign of the *D*-parameter had to be altered. Indeed, a refit of magnetic data confirmed this solution. This fact is very important in getting new magnetostructural *D*-correlations for tetracoordinate Co(II) complexes.

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References

[1] Titiš, J., Boča. R., Inorg. Chem., **49**, 3971-3973 (2010).
[2] Titiš, J., Boča. R., Inorg. Chem., **50**, 11838-11845 (2011).