HFEP Investigation of the Electronic Properties of $S = 1$ Tetrahedral and Octahedral Ni(II) Complexes Containing the Imidodiphosphinate Family of Ligands

E. Ferentinos, D. Maganas, P. Kyritsis (U. of Athens, Greece, Chemistry); J. Krzystek (NHMFL)

Introduction

Ever since their synthesis was reported some thirty years ago, the chalcogenated imidodiphosphinate family of ligands, LH = \((XPR_2)(YPR_2)\)NH, R, R = Ph, 'Pr, have received much attention in the coordination chemistry of both main group and transition metal centers. The deprotonated \(L^-\) ligands are ideal chelating agents to form tetrahedral ML\(_2\) complexes [1]. Following a recent investigation of \(S = 3/2\) tetrahedral CoL\(_2\) complexes by EPR spectroscopy [2], we have undertaken a study of a series of \(S = 1\) tetrahedral NiL\(_2\) and octahedral [NiL\(_2\)(dmf)\(_2\)] complexes. More specifically, the literature-known tetrahedral [Ni\(_i\)(SPR\(_2\))N\(_2\)] [3,4] and [Ni\(_i\)(SePPr\(_2\))N\(_2\)] [5], as well as the novel tetrahedral [Ni\(_i\)(OPPh\(_2\))(SePPh\(_2\))N\(_2\)] and octahedral [Ni\(_i\)(OPPh\(_2\))(SePPh\(_2\))N\(_2\)]\(_\text{as is}\) complexes were investigated by High-Frequency and -Field Electron Paramagnetic Resonance (HFEP) spectroscopy, in an attempt to get insight into their electronic properties.

Experimental

The reaction of the K[\((OPPh_2)(SePPh_2)N\)] ligand with NiCl\(_2\).6H\(_2\)O afforded dark green [Ni\(_i\)(OPPh\(_2\))(SePPh\(_2\))N\(_2\)]\(_\text{as is}\), which, in the presence of dimethylformamide (dmf), was transformed to yellow crystalline [Ni\(_i\)(OPPh\(_2\))(SePPh\(_2\))N\(_2\)]\(_\text{as is}\). The EPR experiments were performed using the EMR Facility and, in particular, its 15/17 T superconducting magnet.

Results and Discussion

All three tetrahedral complexes of Ni(II) proved to be ‘EPR-silent’ in the frequency and field range available (up to 700 GHz, and 14.5 T). However, the octahedral [Ni\(_i\)(OPPh\(_2\))(SePPh\(_2\))N\(_2\)]\(_\text{as is}\) complexes delivered a fairly strong response (Figure 1). The spectrum of the polycrystalline material, although characteristic for a triplet \((S = 1)\) spin state, is uninterpretable due to the structure originating from single crystallites, showing up as a “quasi-noise” (top, green trace). On the other hand, grinding the sample decreased the crystallite size sufficiently to allow at least a preliminary interpretation (black trace). Alternatively, the spectrum can be simulated using positive zero-field-splitting (zfs, red trace), or negative zfs (blue trace). In the first case, however, the simulated low-field \(\Delta M_S = 2\) transition is off by 0.7 T, which makes us believe that the parameter \(D\) is negative, and the experimental spectrum is closer to that obtained for a single crystal due to a field-induced torquing effect (cyan trace).

Conclusions

The work provides evidence that in all tetrahedral Ni(II) complexes, the zfs parameter \(D\) is rather large, as it is expected to exceed 25 cm\(^{-1}\). The electronic properties of [Ni\(_i\)(OPPh\(_2\))(SePPh\(_2\))N\(_2\)]\(_\text{as is}\) and related Ni(II) octahedral complexes will be further investigated by HFEP and other appropriate experimental and theoretical methods.

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References


Figure 1. EPR spectrum of polycrystalline complex [Ni\(_i\)(OPPh\(_2\))(SePPh\(_2\))N\(_2\)]\(_\text{as is}\) 'as is' (top, green trace) and ground (black trace) at 295.2 GHz and 10 K. The red trace is a powder simulation using spin Hamiltonian parameters: \(S = 1, D = +5.7\) cm\(^{-1}\), \(E = 0, g_{xx} = 2.18, g_{zz} = 2.18\) (arbitrary); blue trace: \(S = 1, D = -3.27\) cm\(^{-1}\), \(E = 0, g_{xx} = 2.28, g_{zz} = 2.28\) (arbitrary); cyan trace: single crystal simulation with negative \(D\) and \(B_{||z}\). The g = 2 resonance in the black trace is due to a radical induced by grinding, and is not reproduced in simulation.