Probing the Zero-field Splitting of Tetrahedral *S* = 3/2 Co(II) and *S* = 1 Ni(II) Complexes by Far-InfraRed Magnetic Spectroscopy (FIRMS)

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Introduction

Considerable efforts are currently being taken to accurately determine the magnitude of zero-field splitting (zfs) in 3d-metal-based complexes, by employing a host of experimental techniques [1]. This is due to the importance of zfs in shaping the magnetic properties of either poly- or mono-nuclear complexes, collectively termed single-molecule magnets (SMMs), by imparting on them magnetic anisotropy, which, under certain conditions, ensures slow relaxation of magnetization due to an energy barrier for its reversal [2]. This work aims to accurately determine the zfs of tetrahedral *S* = 3/2 [Co{(EP^{i}Pr$_2$)$_2$N}$_2$], E = S (**1**), Se (**2**) and *S* = 1 [Ni{(EP^{i}Pr$_2$)$_2$N}$_2$], E = S (**3**), Se (**4**), complexes, by employing the FIRMS capacity at the NHMFL. Complexes **1**-**4** contain tetrahedral ME_4 coordination spheres, M = Co, Ni; E = S, Se, respectively, and, among them, **1** and **2** have already been shown to exhibit properties akin to those of SMMs [3].

Experimental

The FIRMS experiments were performed at the DC Facility of the NHMFL using the SCM-3 magnet.

Results and Discussion

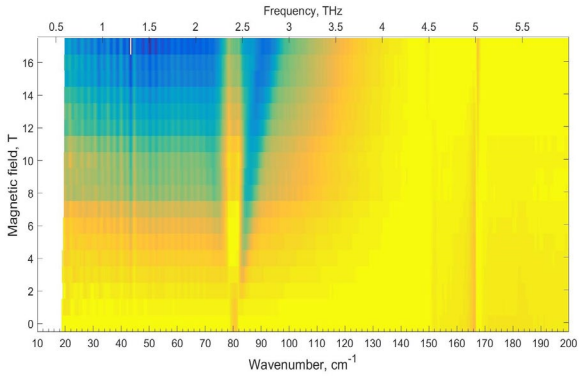

Fig.1 FIR transmission contour plot of complex **3**, showing a single zero-field transition at 80.5 cm^{-1}.

FIRMS spectra of complexes **1** and **2** revealed a single zero-field transition, as expected for an *S* = 3/2 system, at 64 and 67 cm^{-1}, respectively. From these spectra, assuming the zfs tensor to be axial, values of |*D*| = 32.0 and 33.5 cm^{-1}, are obtained for **1** and **2**, respectively, which are in very good agreement with earlier magnetometric data (**Table I**). In addition, a single zero-field transition was also observed for complex **3** at 80.5 cm^{-1}, which for an *S* = 1 system, points at the axial symmetry of its zfs tensor, also confirming earlier magnetometric data [4] (**Table I**). On the other hand, under the experimental conditions employed, complex **4** showed no magnetic FIRMS transitions, despite the fact that a value of |*D*| = 45.4 cm^{-1} has been previously determined [5]. The zfs values of complexes **1**-**4** are collected in **Table I**.

Conclusions

The zfs of tetrahedral complexes **1**-**4** was accurately determined by FIRMS. A very good agreement between the values determined by magnetometry and FIRMS is noted. These data are of interest in the context of magnetostructural correlations concerning these complexes, especially with respect to effects on the zfs of 3d-metal complexes imparted by M−Se versus M−S coordination. Moreover, the accurate zfs data of **Table I** obtained by FIRMS provide benchmark values for related computational studies.

Table I Values of |*D*| for complexes **1**-**4**, determined by magnetometry or FIRMS.

Complex	|*D*| (cm^{-1}) (Magnetometry)	|*D*| (cm^{-1}) (FIRMS)
1	30.5 [3]	32.0 (this work)
2	30.4 [3]	33.5 (this work)
3	77 [4]	80.5 (this work)
4	43.4 [5]	45.4 [5]

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