

## Direct Observation of Fine Structure Transitions in a Paramagnetic Nickel(II) Complex Using Far-Infrared Magnetic Spectroscopy: A New Method for Studying High-Spin Transition Metal Complexes

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Novel far-infrared (FIR) absorption spectroscopy in conjunction with multiple, fixed external magnetic fields (FIR magnetic spectroscopy, FIRMS) has been used to investigate pseudotetrahedral complexes with the formula  $M(PPh_3)_2Cl_2$  (M = Ni, Zn; Ph = C<sub>6</sub>H<sub>5</sub>). Crystal structures have been reported for the Ni complex; we report the structure of the Zn complex. Transmission spectra at 5 K of Ni- $(PPh_3)_2Cl_2$  (S = 1) at zero magnetic field exhibit absorption bands at 11.41, 15.28, and 23.0 cm<sup>-1</sup>. The two lower frequency bands show great sensitivity to external magnetic field, and their field dependence is as expected for electron spin transitions allowing precise determination of the following parameters: |D| =13.35(1) cm<sup>-1</sup>, |E| = 1.93(1) cm<sup>-1</sup>,  $g_{xy} = 2.20(1)$ ,  $g_z = 2.00(1)$ . Corresponding spectra of  $Zn(PPh_3)_2Cl_2$  (S = 0) exhibit bands only at >20 cm<sup>-1</sup>, which show no field dependence. FIRMS is a promising technique for direct investigation of the electronic structure of high-spin transition metal complexes.

Electron paramagnetic resonance (EPR) is widely employed in the study of transition metal ion complexes, particularly those with Kramers (half-integer) spin ground states.<sup>1</sup> Complexes with non-Kramers (integer) spin states, however, are often difficult to study by conventional EPR, due to the effects of zero-field splitting (zfs). Within the past few years, high-frequency and -field EPR (HFEPR) has overcome some of these difficulties,<sup>2</sup> by the use of frequencies venturing into the far-infrared (FIR) region (up to 700 GHz) combined with high magnetic fields (up to 25 T). Field-

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swept HFEPR spectra and analysis have recently been reported for many integer (high) spin transition metal ions for which conventional EPR is unsuitable. These include V(III),<sup>3</sup> Cr(II),<sup>4</sup> Mn(III),<sup>5–7</sup> Fe(II),<sup>8</sup> and Ni(II).<sup>9–11</sup> A complementary method to study such complexes depends on sweeping the frequency while keeping the magnetic field at zero or some fixed value. This technique was originated by Richards and co-workers using a far-IR Michelson interferometer<sup>12,13</sup> and also employed by Champion and co-workers.<sup>14,15</sup> Despite the initial success of these studies, which included studies of metalloproteins such as deoxy-hemoglobin (Fe(II),  $3d^6$ , S = 2) in frozen solution, <sup>15</sup> far-IR magnetic spectroscopy (FIRMS) has not been subsequently pursued, presumably due to low sensitivity and generally inadequate technology. However, with the recent development of spectroscopy based on coherent, monochromatic, frequency-

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tunable radiation sources (backward wave oscillators) operating in the millimeter/submillimeter wavelength region,<sup>16</sup> there now exists a powerful method to study paramagnetic transition metal complexes.<sup>16,17</sup> This modern FIRMS allows recording transmission (or reflection, etc.) spectra at 1.5– 300 K using an optical configuration over the range 40– 1,200 GHz ( $\lambda = 7.5-0.25$  mm) and at fields currently up to 7 T.<sup>18</sup>

We introduce here an application of FIRMS in the area of coordination chemistry, specifically to study the complex Ni(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (Ph = phenyl), which contains pseudotetrahedral Ni(II) (3d<sup>8</sup>, S = 1) and is totally "EPR-silent" using conventional fields and frequencies. We have recently reported a detailed HFEPR study on this compound in the solid state,<sup>11</sup> which, combined with earlier magnetic,<sup>19</sup> optical,<sup>20</sup> and structural studies,<sup>21</sup> allowed a complete description of the electronic structure of the Ni(II) ion. Of particular importance are the spin Hamiltonian parameters determined primarily by HFEPR:  $D = +13.20 \text{ cm}^{-1}$ ,  $|E| = 1.85 \text{ cm}^{-1}$ , isotropic g = 2.20.<sup>11</sup>

To facilitate spectral interpretation of the paramagnetic Ni-(II) complex, we also applied FIRMS to a diamagnetic analogue, Zn(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, as a control. This Zn(II) complex had not, despite having been reported many years ago,<sup>22</sup> been structurally characterized. Crystals of Zn(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> were grown from 1-butanol solution,<sup>23</sup> and the structure was determined by X-ray crystallography.24 As expected, Zn- $(PPh_3)_2Cl_2$  is a pseudotetrahedral complex ( $C_{2v}$  symmetry about Zn), structurally similar to Ni(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (see Figure S1, Supporting Information). A detailed comparison of the two structures is beyond the scope of this paper; however, we note that the P-Ni-P and Cl-Ni-Cl bond angles are very different (111.5° and 128.0°, respectively<sup>21</sup>), while the P-Zn-P and Cl-Zn-Cl bond angles are very similar (115.0  $\pm$  0.2°), due to the absence of ligand-field effects in 3d<sup>10</sup> Zn(II).

Transmission coefficient spectra were recorded on pressed plane-parallel pellets ( $\sim 100 \text{ mg}$ ; diameter, 10 mm; thickness, 1.5-1.8 mm) of M(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (M = Ni, Zn) at zero external magnetic field, and at fixed fields up to 7 T, over the temperature range 5–300 K.<sup>18</sup> The spectra contain shallow oscillations due to constructive and destructive interference of the radiation inside the plane pellet, which acts as a Fabry–Perot resonator. These oscillations are easily modeled

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- (23) Microcrystalline material needed for FIRMS (~100 mg) was conveniently prepared by addition of anhydrous ZnCl<sub>2</sub> in diethyl ether to PPh<sub>3</sub> in benzene (1:2 mol ratio).
- (24) Data collected at 25 °C; colorless crystal; monoclinic *P*21/*c*; a = 11.816(7) Å, b = 17.205(7) Å, c = 16.940 Å,  $\beta = 104.55(4)^\circ$ , V = 3333(3) Å<sup>3</sup>; Z = 4; R = 0.085;  $R_w = 0.101$ ; GOF = 2.80.



**Figure 1.** Transmission coefficient spectra of plane parallel pellets of  $M(PPh_3)_2Cl_2$  (M = Ni,  $\bullet$ ; M = Zn,  $\triangle$ ) at 5 K and zero magnetic field. The inset magnifies the bands seen at 11.41 and 15.28 cm<sup>-1</sup>. Shallow periodic oscillations are due to interference within the pellets;<sup>26</sup> absorption bands are deeper minima and are fit by Lorentzian terms.<sup>18,25</sup>

using well-known optical principles.<sup>25,26</sup> Absorption bands, of whatever origin (vibrational, electronic, ferromagnetic resonance, etc.), are easily seen as deeper minima.

Ni(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> at 5.5 K exhibited a strong, relatively broad band at 23.0(1) cm<sup>-1</sup>, and two narrow, weaker bands at 11.41(2) and 15.28(2) cm<sup>-1</sup> (Figure 1). At higher temperatures, the band at 23 cm<sup>-1</sup> broadened and shifted to slightly higher frequencies, (see Figure S2) but was not affected by application of an external magnetic field. In contrast, the bands at 11.41 and 15.28 cm<sup>-1</sup> showed very little temperature dependence of frequency, but very strong field dependence (see later). Comparison with the zfs parameters determined by HFEPR for Ni(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> allows assignment of these two bands to the transitions with energies, |D| - |E| and |D| +|E| in zero-field,<sup>11</sup> yielding |D| = 13.35(1) cm<sup>-1</sup>, |E| =1.93(1) cm<sup>-1</sup>. While the agreement between HFEPR and FIRMS techniques is excellent, the latter is more accurate, given that it is a true zero-field measurement.

The Zn(II) complex at 5.5 K exhibited two absorption bands, 24.0(1) cm<sup>-1</sup> (Figure 1) and 34.0(1) cm<sup>-1</sup> (not shown), but none at lower frequency. The temperature dependence of the band at 24.0 cm<sup>-1</sup> was essentially the same as that of the corresponding band for the Ni(II) complex (see Figure S2). Lacking knowledge of the crystal and molecular structure of these two complexes over the 5–300 K range, we dare not propose a reason for the modest shift to higher frequency with increasing temperature. The similarity in behavior, however, suggests a common origin for the band. A simple molecular mechanics calculation<sup>27</sup> suggested that torsional modes involving primarily the multiple phenyl rings occur at the following frequencies: 10, 24, and 33–40 cm<sup>-1</sup>.<sup>28</sup> Few studies have been done on very low frequency (<100 cm<sup>-1</sup>) modes in molecular complexes; acetanilide has

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**Figure 2.** Magnetic field dependence of magnetic absorption bands in the transmission spectra of a Ni(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> pellet at 5 K; spectra for Zn-(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> showed no effect of magnetic field. Absorption lines are highlighted by arrows and are labeled with the field value. Experimental points are given by open circles ( $\bigcirc$ ) for B = 0 T, by solid circles ( $\bigcirc$ ) (3 T), and by triangles ( $\triangle$ ) (4 T). The lines show fits using Lorentzians for the absorption bands. At higher fields, the band at ~11 cm<sup>-1</sup> broadens and splits while that at ~15 cm<sup>-1</sup> moves to higher frequencies.

been studied somewhat, as a model for polypeptides,<sup>29,30</sup> but a detailed neutron scattering study on acetanilide assigned a band at 27 cm<sup>-1</sup> to a torsional mode of the single phenyl ring.<sup>30,31</sup> We thus assign the bands observed at 23–24 cm<sup>-1</sup> in M(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> to vibrational modes, possibly involving the phenyl rings.

Application of external magnetic fields, using a Voigt configuration, confirmed the zero-field assignment. Fields up to 7 T at a given temperature had no effect on the spectrum of Zn(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, nor was the band at 23 cm<sup>-1</sup> in Ni(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> affected. However, as shown in Figure 2, the bands for Ni(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> at 11.41 and 15.28 cm<sup>-1</sup> were strongly affected: shifting and splitting and/or broadening significantly with field. The field dependence of the bands is nonlinear, which is as expected for a rhombic, non-Kramers spin system.<sup>11</sup> This can be seen more easily in Figure 3, which presents the electronic spin transition energies as a function of field. The transitions are identified by the formalism for spin triplets.<sup>32</sup> Both the |D| - |E| and |D| + |E| branches are shown; not shown is the branch originating at 2|E| = 3.8(1) cm<sup>-1</sup>. No transitions within this branch were observed here, nor previously by HFEPR.<sup>11</sup> probably due to their low intensities. For D > 0, as determined by HFEPR, the 2|E| zero-field transition originates from an excited state with a Boltzmann population at 5.5 K that is  $\sim 20 \times$  smaller than the ground state.

The calculated lines in Figure 2 used  $|D| = 13.347 \text{ cm}^{-1}$ ,  $|E| = 1.932 \text{ cm}^{-1}$ ,  $g_{x,y} = 2.20$ ,  $g_z = 2.00$ . The zfs values are



**Figure 3.** Magnetic field dependence of far-IR bands for Ni(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> at 5.5 K. Experimental resonances are given by circles ( $\bullet$ ) (*z* transitions), squares ( $\blacksquare$ ) (*x*), and triangles ( $\blacktriangle$ ) (*y*); error bars are within these. The lines represent magnetic resonance transitions calculated for *S* = 1 with *D* = +13.347 cm<sup>-1</sup>, *E* = 1.932 cm<sup>-1</sup>, *g<sub>xy</sub>* = 2.20, *g<sub>z</sub>* = 2.00. The solid lines are for the magnetic field along the molecular *z* axis, the long dashed lines along *x*, and the short dashed lines along *y*. The transitions are also identified by the standard nomenclature for triplet systems with rhombic symmetry.<sup>32</sup>

taken directly from the zero-field FIRMS spectrum; the  $g_{x,y}$  value was taken from HFEPR<sup>11</sup> and gives good agreement with the observed field-dependent transitions. Use of  $g_z = 2.00 \pm 0.01$  fit the FIRMS B<sub>3z</sub> transition better than did use of  $g_z = 2.20$  from HFEPR. The  $g_z$  value in integer-spin systems can sometimes be difficult to determine by HFEPR as *z* transitions are much weaker than *x*, *y* transitions in powder pattern spectra.<sup>5</sup>

We have used FIRMS for the first time to record resonant absorptions in the millimeter/sub-millimeter wavelength range in a high-spin non-Kramers molecular paramagnet. Excellent agreement of the field and temperature behavior of the observed transitions with calculations allowed us to differentiate them into magnetic transitions within the Ni-(II) triplet spin system, and molecular vibrational transitions within the ligands. FIRMS thus represents a technique for the direct measurement of electronic parameters in high-spin transition metal complexes, particularly in determining zfs parameters to high precision, but also g values. One should therefore consider adding FIRMS to the armamentarium of physical methods in inorganic chemistry, along with well established techniques such as (HF)EPR and magnetic measurements including MCD, as well as new methods such as inelastic neutron scattering (INS).<sup>33</sup>

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**Supporting Information Available:** Crystallographic information file and tables of bond distances and angles for Zn(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>. Figure showing the molecular structures of Ni(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> and Zn(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>. Figure showing temperature dependent FIRMS spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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<sup>(31)</sup> This study and a far-IR study<sup>29</sup> also identified bands in this region as arising from translational or librational modes, which might be the case here as well, and crystal lattice changes might be the source of the temperature dependence of these bands.

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