Electronic Properties of Iron(II) Complexes of 2-(Pyridin-2-yl)Benzoxazole

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ABSTRACT

The ligand of 2-(pyridin-2-yl)benzoxazole (pbo) has been prepared, and the corresponding complexes of iron(II), the tetrafluoroborate, perchlorate, and tetraphenylborate, have been synthesized and characterized in details in magnetism, Mössbauer, and electronic spectral properties. It was found that the tetrafluoroborate and perchlorate were observed to be normal paramagnet, with the magnetic moment of 5.29 BM (θ = -6K) for the perchlorate and 5.06 BM (θ = -9K) for the tetrafluoroborate complexes at room temperature. For the tetraphenylborate complex, the magnetic moment was found to be 5.20-5.50 BM (at room temperature), which was slightly and gradually decreased to 4.25-4.57 BM at low temperature (90K), however. This is associated with the spin-state transition in iron(II) for this salts as indicated by its Mössbauer spectral properties. The electronic spectrum of the corresponding nickel complex showed that the ligand field strength lied in the range for which the iron(II) complex might undergo the spin-state transition.

Keywords: spin-state transition, iron(II), pbo, tetraphenylborate, nickel(II)

1. INTRODUCTION

Research in a spin-state transition of iron(II) complexes has very rapidly progressed, and now this research is directed to obtain material samples that can be potentially applied as switches data storage devices and also optical displays. It is because of the inherent bi-stability of high spin and low spin states of iron(II) which leads to changes in the major magnetic materials and usually the color [1]. As in electrical-molecular switches, a mechanism of turning-ON and -OFF is required, and it may be achieved with the abrupt spin transitions with hysteresis. Smaller units (such as molecules) exhibiting bistability and thermal hysteresis are required for the size of data storage devices to be reduced while the capacity of them increased [1-4]. Accordingly, the primary research goal is then to develop new materials where the spin crossover (SCO) response time can be decreased from nanoseconds to femtoseconds. One of the advantages of the SCO phenomena is the absence of fatigue because there is an intra-electronic transition instead of an electron displacement through space. Thus, SCO materials are particularly attractive for potential applications in molecular sensing, switching, data storage, display, and
other electronic devices at a nanometric scale [5]. Indeed, samples satisfying this response were readily observed, unfortunately they exhibit abrupt-hysteresis at quite low temperatures, for example as in iron(II)-complexes of bpp [Fe(bpp)₂]₂(X=BF₄, CF₃SO₃) [6,7,8,9,10] and above room temperatures as in iron(II)-complexes of 1,2,4-triazole [11,12,13]. For these, it might not be easily suitable goal without modification. Quite recently abrupt but no hysteresis was reported by Atwood et al. [14]. Thus, attempts have been continually done to produce the SCO system which is suitable for the application.

The stability of low-versus high-spin states of iron(II) complexes has been interpreted by ligand field theory, which is a perturbation theory of the electron-electron interaction of metal-ligands. Thus, back to a long time ago, it has been generally observed that the coordinating agent of nitrogen donor atom in five-member ring leads to lower ligand field strength compared to that in a six-membered ring. Thus, studies have been undertaken for salts of the tris(2-(pyridin-2-yl)benzimidazole) iron(II) ion, [Fe(pbi)₃]²⁺ [15,16,17,18]. For this system, the singlet →quintet change is displaced to lower temperatures. The increased stabilization of the quintet state presumably results from the steric and electronic effects of the fused benzene ring. This could be expected to hinder the close approach of the metal atom necessary for spin-pairing and to introduce additional inter-ligand repulsive interactions.

The related structure of pbi is 2-(pyridin-2-yl)benzothiazole, pbt (X=S) [Figure 1], which has been studied earlier [19] and [Fe(pbt)₃](BPh₄)₂ has been shown to display a spin transition in a solid state. Because of relatively low stability, this system is unsuitable for solution studies. In further attempt to obtain a system suitable for comparative study the ligand 2-(pyridin-2-yl)benzoxazole, pbo (X=O) [Figure 1], has been synthesized and its complexes are considered in this section. It will allow a direct consideration of the effect of replacement of sulfur by oxygen in a five-membered heterocycle on the electronic properties of the iron(II) complexes. The importance of pbo in the complex of Cu(II) has been studied in DNA interaction as antioxidation and in vitro cytotoxicity [20]. While the photophysical role of complexes of pbo has been observed in Os(II) [21].

2. MATERIALS AND METHODS

2.1 Materials

The main chemicals, 2-thiopicolylamide, o-aminophenol, FeCl₂.4H₂O, NiClO₄.6H₂O, NaBF₄, NaClO₄, and NaBPh₄ were purchased from Sigma-Aldrich. All the reagents were used without initial purification.

2.2 Preparation of Ligand, pbo

A mixture of 2-thiopicolylamide (2.76 g) and o-aminophenol (2.18 g) was heated together at about 170°C until the evolution of gases ceased (approx.72 hours). The resultant mixture was extracted into ethanol, treated with activated charcoal then diluted with water after that a light-yellow product was obtained. This was recrystallized from petroleum ether (60-80°C). (needles, m.p. 104-106°C; 105-106°C [22]).

2.3 Preparation of the Complex, [Fe(pbo)₃](X)₂ (X = BF₄, ClO₄, BPh₄), and [Ni(pbo)₃](ClO₄)₂

To a warm ethanolic solution of free ligand, pbo (3x moles) was added a warm aqueous solution of iron(II) chloride tetrahydrate (1x mole). A hot aqueous solution of the appropriate sodium salt (either tetrafluoroborate, perchlorate, or tetraphenylborate) was then added whereupon
the complex salt crystallized. All the reactions were performed in nitrogen atmosphere. The product was collected, washed with cold water and then dried in vacuo over P₂O₅.

The corresponding complex of [Ni(pbo)₃](ClO₄)₂ was obtained by direct interaction of the free ligand pbo (3x moles) with nickel perchlorate hexahydrate (1x mole) in ethanolic solution. The lilac crystalline solid was collected, washed with ethanol and dried in vacuo over P₂O₅.

2.4 Physical Measurements

Magnetic measurements. The magnetic data for solid samples were obtained using a Newport Variable Temperature Gouy Balance calibrated with CoHg(NCS)₄. All data presented in the table have been corrected for diamagnetism calculated using Pascal’s constants [23]. Curie-Weiss θ values refer to the expression \(\chiM' = C/(T-\theta)\) and were obtained from an extrapolation of 1/\(\chiM'\) against T. Molar susceptibilities (\(\chiM'\)) are quoted in m³ mol⁻¹ and the magnetic moments were calculated according to the relation: \(\mu\text{eff} = 798(\chiM')^{1/2}\).

Mössbauer spectra. Mössbauer Spectra were measured with spectrometer operating in the time mode equipped with a room-temperature \(^{57}\)Co source in a palladium matrix and calibrated with metallic iron foil. For variable temperature measurements, a special brass reflectance attachment with silica glass windows was used and this was placed in contact with cylinder of liquid held at constant temperature. For low-temperature measurements, dry nitrogen gas was passed over the assembly.

Elemental analysis. Analyses for carbon, hydrogen, and nitrogen of the ligand were carried out in the microanalytical laboratory, and the metal content of the complexes was estimated after the complexes were decomposed by fuming with sulfuric acid followed by direct ignition to Fe₂O₃ for iron content. The nickel content was determined gravimetrically as a complex of bis(dimethylglyoximato)nickel(II) [24]. The analysis results of the ligand and its complexes together with colors are listed in Table 1.

Table 1. Elemental analysis of pbo and its complexes (Note: Found figures are given below the calculated ones).

<table>
<thead>
<tr>
<th>Species</th>
<th>color</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>M</th>
</tr>
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<tr>
<td>pbo</td>
<td>light yellow</td>
<td>73.46</td>
<td>4.11</td>
<td>14.28</td>
<td></td>
</tr>
<tr>
<td><a href="BPh%E2%82%84">Fe(pbo)₃</a>₂</td>
<td>yellow-orange</td>
<td>78.64</td>
<td>5.03</td>
<td>6.55</td>
<td>4.35</td>
</tr>
<tr>
<td><a href="BF%E2%82%84">Fe(pbo)₃</a>₂·1.5H₂O</td>
<td>yellowish</td>
<td>78.76</td>
<td>4.70</td>
<td>6.65</td>
<td>4.54</td>
</tr>
<tr>
<td><a href="ClO%E2%82%84">Fe(pbo)₃</a>₂·1H₂O</td>
<td>yellowish</td>
<td>51.11</td>
<td>2.71</td>
<td>9.76</td>
<td>6.65</td>
</tr>
<tr>
<td><a href="ClO%E2%82%84">Fe(pbo)₃</a>₂·0.5H₂O</td>
<td>pale-lilac</td>
<td>50.55</td>
<td>2.94</td>
<td>9.82</td>
<td>6.86</td>
</tr>
<tr>
<td><a href="ClO%E2%82%84">Ni(pbo)₃</a>₂·0.5H₂O</td>
<td></td>
<td>50.10</td>
<td>2.46</td>
<td>9.41</td>
<td>6.76</td>
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</table>
3. RESULTS AND DISCUSSIONS

3.1 Preparation of pbo

The compound of 2-(pyridin-2-yl)benzoxazole, pbo, has been known for some time and has been obtained by various methods. Cohen [25] in 1978 synthesized pbo by refluxing o-aminophenol with 2-picolinamide in pyridine solution for about 20 hours. Hisano et al. [22] synthesized pbo by heating a mixture of o-aminophenol, 2-picolinamide and sulfur at 160-170°C for about 10 hours. While in the present work, pbo was synthesized by heating together a mixture of o-aminophenol and 2-picolinthioamide at 180°C until evolution of H₂S gas ceased. The elemental analysis shown in Table 1 signifies the compound of pbo.

3.2 Formula of Complex

The stoichiometric interaction of divalent metal (1x mole) and pbo (3x moles) as ligand should produce the tris-bidentate ligand metal(II) complex, the corresponding elemental analysis shown in Table 1 signifies the empirical formula. Thus, the geometry of octahedral cationic system is then proposed (shown in Figure 2) as to be characterized their properties. It turns out from Figure 2 (LEFT) that this complex cation should adopt the fac-N₆/N₆ isomer or mer-N₆/N₆ isomer (N₆ = N_pyridine, N₆ = N_benzoxazole). It also can be understood that the coordinating agent of the two differen N-donor atoms might cause to distinct distortion.

3.3 Magnetism

For the yellow-orange tris(ligand)iron(II) complexes, [Fe(pbo)₃]X₂ (X=ClO₄, BF₄, and BPh₄) which have been prepared, the two [Fe(pbo)₃] (ClO₄)₂ and [Fe(pbo)₃](BF₄)₂ have magnetic moments normal for high-spin iron(II) (Table 2) at least down to 99K, with the moment 5.29BM (θ = -6K) for the perchlorate and 5.06 BM (θ = -9K) for the tetrafluoroborate at

Table 2. Magnetic data (μeff) for complexes of pbo in various temperature (K), χM in m³ mol⁻¹.

<table>
<thead>
<tr>
<th>Complex</th>
<th>T/K</th>
<th>10⁶ χM</th>
<th>μeff/BM</th>
<th>T/K</th>
<th>10⁶ χM</th>
<th>μeff/BM</th>
<th>T/K</th>
<th>10⁸ χM</th>
<th>μeff/BM</th>
<th>T/K</th>
<th>10⁸ χM</th>
<th>μeff/BM</th>
</tr>
</thead>
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<tr>
<td><a href="BPh%E2%82%84">Fe(pbo)₃</a>₂</td>
<td>303</td>
<td>1605</td>
<td>5.58</td>
<td>295</td>
<td>1453</td>
<td>5.22</td>
<td>303</td>
<td>1471</td>
<td>5.34</td>
<td>303</td>
<td>1484</td>
<td>5.36</td>
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<tr>
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<td>89</td>
<td>3674</td>
<td>4.57</td>
<td>99</td>
<td>2874</td>
<td>4.25</td>
<td>99</td>
<td>4198</td>
<td>5.14</td>
<td>99</td>
<td>4440</td>
<td>5.29</td>
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<tr>
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<td>99</td>
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<td>4.60</td>
<td>118</td>
<td>2584</td>
<td>4.42</td>
<td>118</td>
<td>3579</td>
<td>5.20</td>
<td>137</td>
<td>3252</td>
<td>5.33</td>
</tr>
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<td><a href="BPh%E2%82%84">Fe(pbo)₃</a>₂</td>
<td>118</td>
<td>2959</td>
<td>4.72</td>
<td>137</td>
<td>2360</td>
<td>4.54</td>
<td>137</td>
<td>3129</td>
<td>5.23</td>
<td>176</td>
<td>2511</td>
<td>5.33</td>
</tr>
<tr>
<td><a href="BPh%E2%82%84">Fe(pbo)₃</a>₂</td>
<td>137</td>
<td>2655</td>
<td>4.82</td>
<td>157</td>
<td>2163</td>
<td>4.64</td>
<td>176</td>
<td>2511</td>
<td>5.31</td>
<td>176</td>
<td>2908</td>
<td>5.37</td>
</tr>
<tr>
<td><a href="BPh%E2%82%84">Fe(pbo)₃</a>₂</td>
<td>157</td>
<td>2426</td>
<td>4.92</td>
<td>176</td>
<td>2051</td>
<td>4.80</td>
<td>176</td>
<td>2090</td>
<td>5.36</td>
<td>255</td>
<td>1799</td>
<td>5.40</td>
</tr>
<tr>
<td><a href="BPh%E2%82%84">Fe(pbo)₃</a>₂</td>
<td>176</td>
<td>2259</td>
<td>5.04</td>
<td>196</td>
<td>1967</td>
<td>4.95</td>
<td>176</td>
<td>1763</td>
<td>5.35</td>
<td>255</td>
<td>1579</td>
<td>5.44</td>
</tr>
<tr>
<td><a href="ClO%E2%82%84">Ni(pbo)₃</a>₂</td>
<td>196</td>
<td>2122</td>
<td>5.15</td>
<td>216</td>
<td>1818</td>
<td>5.00</td>
<td>216</td>
<td>1818</td>
<td>5.00</td>
<td>255</td>
<td>1579</td>
<td>5.44</td>
</tr>
<tr>
<td><a href="ClO%E2%82%84">Ni(pbo)₃</a>₂</td>
<td>216</td>
<td>2000</td>
<td>5.24</td>
<td>235</td>
<td>1752</td>
<td>5.12</td>
<td>216</td>
<td>2000</td>
<td>5.24</td>
<td>255</td>
<td>1579</td>
<td>5.44</td>
</tr>
<tr>
<td><a href="ClO%E2%82%84">Ni(pbo)₃</a>₂</td>
<td>235</td>
<td>1879</td>
<td>5.24</td>
<td>255</td>
<td>1650</td>
<td>5.17</td>
<td>235</td>
<td>1879</td>
<td>5.24</td>
<td>255</td>
<td>1579</td>
<td>5.44</td>
</tr>
<tr>
<td><a href="ClO%E2%82%84">Ni(pbo)₃</a>₂</td>
<td>275</td>
<td>1666</td>
<td>5.40</td>
<td>275</td>
<td>1556</td>
<td>5.22</td>
<td>275</td>
<td>1666</td>
<td>5.40</td>
<td>275</td>
<td>1579</td>
<td>5.44</td>
</tr>
</tbody>
</table>
room temperature. For the tetraphenylborate, the magnetic moment at room temperature is normal for high-spin iron(II) (Sample 1, $\mu_{\text{eff}} = 5.58 \text{ BM}$; Sample 2, $\mu_{\text{eff}} = 5.22 \text{ BM}$), but it decreases with decreasing temperatures. This suggests that this complex undergoes a gradual thermally induced singlet $\leftrightarrow$ quintet spin state transition, the singlet state being accessible only at relatively low temperatures. The data in Table 2 and Figure 3 indicate that this very gradual transition is definitely incomplete at the lower limit of the experimental temperature range. This behavior is similar to that for $[\text{Fe}(\text{pbt})_3](\text{BPh}_4)_2$ [19].

![Figure 3](image_url)

**Figure 3.** Magnetic moment vs temperature for $[\text{Fe}(\text{pbo})_3](\text{BPh}_4)_2$, A. Sample 1; B. Sample 2.

### 3.4 Mössbauer Effect

Support for the postulate of the occurrence of a spin transition was provided by the Mössbauer spectra shown in Figure 4 recorded at room and low temperature (77K). Both the Mössbauer spectra of $[\text{Fe}(\text{pbo})_3](\text{BPh}_4)_2$ enriched with 30% $^{57}$Fe show similar pattern with distinctly asymmetric doublet lines. By the least squares fitting of the data to Lorentzian line shapes, this can be resolved into two doublets, one associated with low-spin iron(II) and the other with high-spin iron(II). The low-spin lines overlap with the low-velocity component of the high-spin doublet giving rise to the apparent asymmetry. The parameters extracted for the two doublets (listed in Table 3) correspond to the areas of high-spin and low-spin fractions to be about 74% and 26%, respectively for the room-temperature spectrum, but about 67% and 33%, respectively for the low-temperature spectrum which is consistent with the magnetic behavior (Table 2, Figure 3). While these area fractions cannot be related directly to the relative concentrations of high-spin and low-spin species because of the expected differences in the Debye-Waller factors for the two spin isomers [26], the increase in the area fraction for the quintet species at room temperature is certainly indicative of an increase in concentration of this species. This is so because the recoil-free fraction for high-spin iron(II) in particular diminishes with increasing temperature especially in a salt such as a tetraphenylborate. Thus, in the absence of a spin transition, a decrease in the area fraction for the high-spin lines would be anticipated. The Mössbauer parameters extracted from the room- and low-temperatures given in Table 3 show temperature dependence, noted for $\Delta E_{\text{Q}}$ for the quintet species is normal. The Mössbauer spectrum suggests that at room
Figure 4. Mössbauer spectra of $[^{57}\text{Fe}(\text{pbo})_3](\text{BPh}_4)_2$ at room temperature (A) and at 77K (B).

Table 3. Mössbauer spectral parameters for $[\text{Fe}(\text{pbo})_3](\text{BPh}_4)_2$.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$\Delta E_Q$ (mm s$^{-1}$)</th>
<th>$\delta_m$ (mm s$^{-1}$)</th>
<th>Spin State</th>
</tr>
</thead>
<tbody>
<tr>
<td>295</td>
<td>1.03</td>
<td>1.32</td>
<td>$^5T_2$</td>
</tr>
<tr>
<td></td>
<td>0.41</td>
<td>0.39</td>
<td>$^1A_1$</td>
</tr>
<tr>
<td>77</td>
<td>1.89</td>
<td>1.64</td>
<td>$^5T_2$</td>
</tr>
<tr>
<td></td>
<td>0.61</td>
<td>0.63</td>
<td>$^1A_1$</td>
</tr>
</tbody>
</table>

At room temperature the bulk $[\text{Fe}(\text{pbo})_3](\text{BPh}_4)_2$ contains the low-spin species.

3.5 Electronic Spectra

Consistent with the occurrence of a thermally induced spin state transition, a marked thermochromism similar to that observed for $[\text{Fe}(\text{pbt})_3](\text{BPh}_4)_2$ [19] was also observed for $[\text{Fe}(\text{pbo})_3](\text{BPh}_4)_2$. At room temperature, the complex is pale orange, but at low temperature, it becomes deep red-orange. The spectra shown in Figure 5(A) reveal that at low temperature the $t_2 \rightarrow \pi^*$ charge transfer transition increases in intensity and moves to lower energy from about 20000 cm$^{-1}$ at room temperature to 18000 cm$^{-1}$ at low temperature (90K), being consistency with the greater occupancy of the $t_2g$ level and the expected reduction in the bond lengths accompanying population of the low-spin species. Again this behavior is quite similar to that observed for $[\text{Fe}(\text{pbt})_3](\text{BPh}_4)_2$, in which the charge transfer absorption occurs at slightly lower wavenumbers. No high-spin ligand field band for $[\text{Fe}(\text{pbo})_3](\text{BPh}_4)_2$, was observed, the charge-transfer band tailing off well into the visible region giving broad, low-intensity absorption.

Unlike $[\text{Fe}(\text{pbo})_3](\text{BPh}_4)_2$, both the complex perchlorate and fluoroborate salts do not exhibit a spin-state transition over the experimental temperature range. For these, a ligand field band is apparent at about 11500 cm$^{-1}$ (Figure 5B-C). This very broad band presumably encompasses the Jahn-Teller split components of the $5T_{2g} \rightarrow 5E_g$ transition. The charge-transfer band appears at about 22000 cm$^{-1}$. The marked difference in
magnetic behavior and electronic spectra for these salts compared with the tetraphenylborate salt indicates a strong anion dependence of the manifestation of the spin transition. This effect has been frequently observed in other systems [27].

The electronic spectrum (in acetone, Figure 6) shows a fairly well-resolved ligand field band which is split into two components centered at about 10500 and 11800 cm\(^{-1}\) \((\varepsilon = 11.5-12.5 \text{ Lmol}^{-1}\text{cm}^{-1})\). This band must arise from \(^5T_{2g} \rightarrow ^3E_g\) transition due to the high-spin species, and the splitting may be due to Jahn-Teller effect [28] or due to arising from low symmetry components to the ligand field. In the charge-transfer region, the spectrum

\[
\begin{array}{c}
\text{Figure 5. Diffuse reflectance spectra of A, } [^{57}\text{Fe}(\text{pbo})_3](\text{BPh}_4)_2, \text{ B, } [\text{Fe}(\text{pbo})_3](\text{BF}_4)_2 \text{ and C, } [\text{Fe}(\text{pbo})_3](\text{ClO}_4)_2. \\
\end{array}
\]

\[
\begin{array}{c}
\text{Figure 6. Electronic spectrum of } [\text{Fe}(\text{pbo})_3](\text{BF}_4)_2 \text{ in acetone solution, } 1.18 \times 10^{-3} \text{ M (A) and } 10^{-2} \text{ M (B).} \\
\end{array}
\]
of \([\text{Fe}(\text{pbo})_3]^{2+}\) shows a similar pattern to that of \([\text{Fe}(\text{pbt})_3]^{2+}\), but a shoulder at about 21000 cm\(^{-1}\) \((\varepsilon = 850 \text{ Lmol}^{-1}\text{cm}^{-1})\) appears more pronounced in the spectrum of the former. The charge transfer band is observed at about 23500 cm\(^{-1}\) \((\varepsilon = 1450 \text{ Lmol}^{-1}\text{cm}^{-1})\), significantly higher wavenumber than that for \([\text{Fe}(\text{pbt})_3]^{2+}\) \((\text{c.f. about 19300 cm}^{-1})\) which may reflect the less pronounced \(\pi\)-acceptor character of benzoxazole systems. The absence of unusual temperature-dependence in this spectrum and the low extinction coefficient suggest that \([\text{Fe}(\text{pbo})_3]^{2+}\) is simple paramagnetic in solution. Unfortunately, the species is somewhat unstable in solution and thus, it is not suitable for a detailed magnetic study in that state.

### 3.6 The Nickel(II) Complex

The corresponding nickel complex, \([\text{Ni}(\text{pbo})_3]^{2+}\) \((\text{ClO}_4)_2\), was characterized to obtain special data for meaningful comparative purposes. For this, the electronic spectrum was recorded both in solid state and acetonitrile solution and an identical pattern is shown for the two (Figure 7). The ligand field band \({}^3A_{2g} \rightarrow {}^3T_{2g}\) and a prominent shoulder to this \({}^3A_{2g} \rightarrow {}^1E_g\) are observed at 11000 cm\(^{-1}\) \((\varepsilon = 6.8 \text{ Lmol}^{-1}\text{cm}^{-1})\) and 12600 cm\(^{-1}\) \((\varepsilon = 4.0 \text{ Lmol}^{-1}\text{cm}^{-1})\), respectively. The second ligand field band, \({}^3A_{2g} \rightarrow {}^3T_{1g}(F)\), occurs about 18000 cm\(^{-1}\) leading to the ratio \(\nu_2 : \nu_1 = 1.64\). The electronic spectrum was recorded both in solid state and acetonitrile solution and an identical pattern is shown for the two (Figure 7). The ligand field band \({}^3A_{2g} \rightarrow {}^3T_{2g}\) and a prominent shoulder to this \({}^3A_{2g} \rightarrow {}^1E_g\) are observed at 11000 cm\(^{-1}\) \((\varepsilon = 6.8 \text{ Lmol}^{-1}\text{cm}^{-1})\) and 12600 cm\(^{-1}\) \((\varepsilon = 4.0 \text{ Lmol}^{-1}\text{cm}^{-1})\), respectively. The second ligand field band, \({}^3A_{2g} \rightarrow {}^3T_{1g}(F)\), occurs about 18000 cm\(^{-1}\) leading to the ratio \(\nu_2 : \nu_1 = 1.64\).

Figure 7. Electronic spectra of \([\text{Ni}(\text{pbo})_3](\text{ClO}_4)_2\) in acetonitrile solution (10\(^{-2}\) M), (A) and in solid state (B).

which is normal for octahedral nickel(II) \([28]\). Confirmation of octahedral symmetry is also reflected in the magnetic moment. At room temperature, the moment is about 3.07 BM \((\theta = -2\text{K})\) which indicates a slight orbital contribution arising from spin-orbit coupling. The ligand field strength \((\nu_1)\) observed for \([\text{Ni}(\text{pbo})_3]^{2+}\) here lies in the range originally predicted to encompass the value leading to the spin-crossover in the corresponding iron(II). In comparison to \(\text{pbt}\) \((\text{c.f. } \nu_1 = 10800 \text{ cm}^{-1}, \varepsilon = 11 \text{ Lmol}^{-1}\text{cm}^{-1})\) for \([\text{Ni}(\text{pbt})_3]^{2+}\) in aqueous acetone, the ligand field strength for \(\text{pbo}\) is thus slightly greater though this comparison is not under strictly comparable conditions.

### 4. CONCLUSION

It can be concluded that within the three salts of \([\text{Fe}(\text{pbo})_3](\text{X})_2\), only the tetraphenylborate exhibits an incomplete gradual spin-state transition in iron(II) with dominant high-spin fraction at room temperature. While the other two, the tetrafluoroborate and the perchlorate salts, were found to be normal high-spin over the experimental temperature range, 90-303 K. Thus, the transition is due to the solid state.
of anionic effects. However, the electronic spectral properties of the corresponding nickel complex show that the ligand field band lies in the range in which the [Fe(pbo)3](X)2 undergoes spin-state transition.

REFERENCES


