



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

Kristian Handoyo Sugiyarto [a] and Harold Andrew Goodwin [b]

[a] Department of Chemistry Education, Yogyakarta State University, Jl. Colombo No.1., Yogyakarta 55281, Indonesia.

[b] The School of Chemistry, University of New South Wales, Australia.

\*Author for correspondence; e-mail: sugiyarto@uny.ac.id

Received: 21 January 2019

Revised: 8 March 2019

Accepted: 23 March 2019

## 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 ( $\theta = -6\text{K}$ ) for the perchlorate and 5.06 BM ( $\theta = -9\text{K}$ ) 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

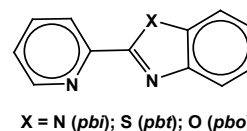
Research in a spin-state transition of iron(II) complexes has very rapidly progressed, and now this research is directed to obtain material samples that can be potentially applied as switches data storage devices and also optical displays. It is because of the inherent bi-stability of high spin and low 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 intralelectronic 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*)<sub>2</sub>](X)<sub>2</sub> (X=BF<sub>4</sub>, CF<sub>3</sub>SO<sub>3</sub>) [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*)<sub>3</sub>]<sup>2+</sup> [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*)<sub>3</sub>](BPh<sub>4</sub>)<sub>2</sub> 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



**Figure 1.** Structure of *pbi*, *pbt*, and *pbo*.

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-thiopicolyamide, *o*-aminophenol, FeCl<sub>2</sub>·4H<sub>2</sub>O, NiClO<sub>4</sub>·6H<sub>2</sub>O, NaBF<sub>4</sub>, NaClO<sub>4</sub>, and NaBPh<sub>4</sub> were purchased from Sigma-Aldrich. All the reagents were used without initial purification.

### 2.2 Preparation of Ligand, *pbo*

A mixture of 2-thiopicolyamide (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*)<sub>3</sub>](X)<sub>2</sub> (X = BF<sub>4</sub>, ClO<sub>4</sub>, BPh<sub>4</sub>), and [Ni(*pbo*)<sub>3</sub>](ClO<sub>4</sub>)<sub>2</sub>

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  $P_2O_5$ .

The corresponding complex of  $[Ni(pbo)_3](ClO_4)_2$  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  $P_2O_5$ .

## 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  $\theta$  values refer to the expression  $\chi_M' = C/(T-\theta)$  and were obtained from an extrapolation of a plot of  $1/\chi_M'$  against  $T$ . Molar susceptibilities ( $\chi_M'$ ) are quoted in  $m^3 mol^{-1}$  and the magnetic moments were calculated according to the relation:  $\mu_{eff} = 798(\chi_M')^{1/2}$ .

*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 cylinder of liquid held

at constant temperature was placed in contact with the sample. Isomer shifts were quoted on the nitroprusside scale and for conversion to the standard iron scale, they were subtracted with  $0.257 mm s^{-1}$ . Mössbauer spectral parameters were extracted from the least squares fitting of the data to Lorentzian line shapes.

*Electronic spectra.* The electronic spectra of complexes in solid and solution were recorded with a Zeiss PMQ II Spectrophotometer. For reflectance spectra, the samples were spread on filter paper. 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  $Fe_2O_3$  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).

Species	color	C	H	N	M
<i>pbo</i>	light yellow	73.46	4.11	14.28	
		73.35	3.98	14.15	
$[Fe(pbo)_3](BPh_4)_2$	yellow-orange	78.64	5.03	6.55	4.35
		78.76	4.70	6.65	4.54
$[Fe(pbo)_3](BF_4)_2 \cdot 1.5H_2O$	yellowish	51.16	3.22	9.95	6.61
		51.11	2.71	9.76	6.65
$[Fe(pbo)_3](ClO_4)_2 \cdot 1H_2O$	yellowish	50.19	3.04	9.76	6.48
		49.90	2.91	9.68	6.37
$[Ni(pbo)_3](ClO_4)_2 \cdot 0.5H_2O$	pale-lilac	50.55	2.94	9.82	6.86
		50.10	2.46	9.41	6.76

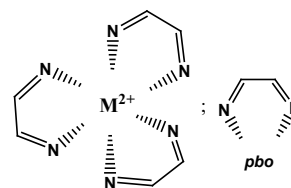
### 3. RESULTS AND DISCUSSIONS

#### 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 H<sub>2</sub>S 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)



**Figure 2.** The proposed octahedral geometry of  $[M(pbo)_3]^{2+}$ .

as to be characterized their properties. It turns out from Figure 2 (LEFT) that this complex cation should adopt the *fac*-N<sub>p</sub>/N<sub>b</sub> isomer or *mer*-N<sub>p</sub>/N<sub>b</sub> isomer (N<sub>p</sub> = N<sub>pyridine</sub>, N<sub>b</sub> = N<sub>benzoxazole</sub>). It also can be understood that the coordinating agent of the two different N-donor atoms might cause to distinct distortion.

#### 3.3 Magnetism

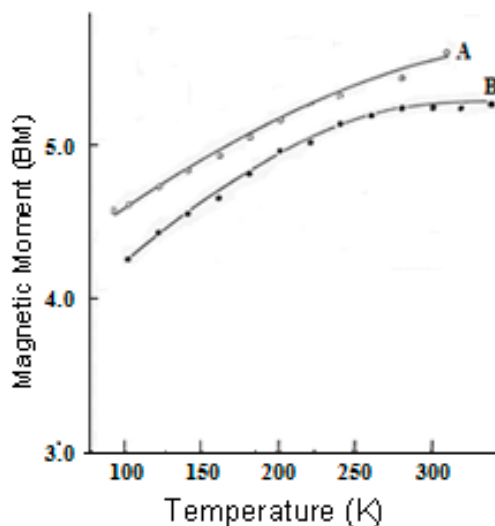
For the yellow-orange tris(ligand)iron(II) complexes,  $[Fe(pbo)_3]X_2$  (X = ClO<sub>4</sub>, BF<sub>4</sub>, and BPh<sub>4</sub>) which have been prepared, the two  $[Fe(pbo)_3]$  (ClO<sub>4</sub>)<sub>2</sub> and  $[Fe(pbo)_3](BF_4)_2$  have magnetic moments normal for high-spin iron(II) (Table 2) at least down to 99K, with the moment 5.29 BM ( $\theta = -6K$ ) for the perchlorate and 5.06 BM ( $\theta = -9K$ ) for the tetrafluoroborate at

**Table 2.** Magnetic data ( $\mu_{\text{eff}}$ ) for complexes of *pbo* in various temperature (K),  $\chi_M$  in m<sup>3</sup> mol<sup>-1</sup>.

$[Fe(pbo)_3](BPh_4)_2$ (Sample 1)			$[^{57}Fe(pbo)_3](BPh_4)_2$ (Sample 2)			$[Fe(pbo)_3](BF_4)_2$ ( $\theta = -9K$ )			$[Fe(pbo)_3](ClO_4)_2$ ( $\theta = -6K$ )		
T / K	$10^{10} \chi_M$	$\mu_{\text{eff}}/BM$	T / K	$10^{10} \chi_M$	$\mu_{\text{eff}}/BM$	T / K	$10^{10} \chi_M$	$\mu_{\text{eff}}/BM$	T / K	$10^{10} \chi_M$	$\mu_{\text{eff}}/BM$
303	1605	5.58	295	1453	5.22	303	1471	5.34	303	1484	5.36
89	3674	4.57	99	2874	4.25	99	4198	5.14	99	4440	5.29
99	3355	4.60	118	2584	4.42	118	3579	5.20	137	3252	5.33
118	2959	4.72	137	2360	4.54	137	3129	5.23	176	2573	5.37
137	2655	4.82	157	2163	4.64	176	2511	5.31	216	2098	5.37
157	2426	4.92	176	2051	4.80	216	2090	5.36	255	1799	5.40
176	2259	5.04	196	1967	4.95	255	1763	5.35	295	1579	5.44
196	2122	5.15	216	1818	5.00	<b><math>[Ni(pbo)_3](ClO_4)_2</math> (<math>\theta = -2K</math>)</b>					
216	2000	5.24	235	1752	5.12	<b>T / K</b>	<b><math>10^{10} \chi_M</math></b>	<b><math>\mu_{\text{eff}}/BM</math></b>	<b>T / K</b>	<b><math>10^{10} \chi_M</math></b>	<b><math>\mu_{\text{eff}}/BM</math></b>
235	1879	5.24	255	1650	5.17	303	487	3.07	216	664	3.02
275	1666	5.40	275	1556	5.22	99	1498	3.07	255	585	3.08
			313	1360	5.21	137	1051	3.03	295	497	3.05
			333	1294	5.24	176	836	3.06			

room temperature. For the tetraphenylborate, the magnetic moment at room temperature is normal for high-spin iron(II) (Sample 1,  $\mu_{\text{eff}} = 5.58$  BM; Sample 2,  $\mu_{\text{eff}} = 5.22$  BM), but it decreases with decreasing temperatures. This suggests that this complex undergoes a gradual thermally induced singlet  $\rightleftharpoons$  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].

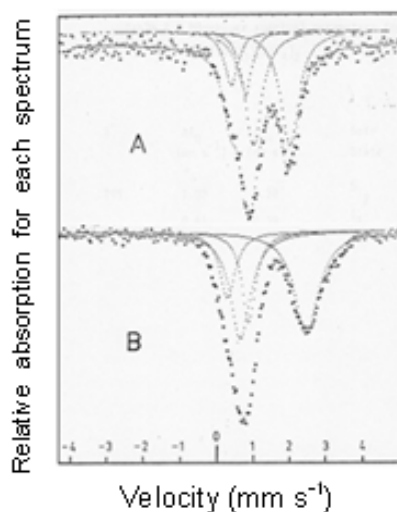


**Figure 3.** Magnetic moment vs temperature for  $[\text{Fe}(\text{pbt})_3](\text{BPh}_4)_2$ , A. Sample 1; B. Sample 2.

### 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  $[\text{Fe}(\text{pbt})_3](\text{BPh}_4)_2$  enriched with 30%  $^{57}\text{Fe}$  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  $\Delta E_Q$  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  $[\text{Fe}(\text{pbo})_3](\text{BPh}_4)_2$ .

T (K)	$\Delta E_Q$ ( $\text{mm s}^{-1}$ )	$\delta_{\text{is}}$ ( $\text{mm s}^{-1}$ )	Spin State
295	1.03	1.32	$^5T_2$
	0.41	0.39	$^1A_1$
77	1.89	1.64	$^5T_2$
	0.61	0.63	$^1A_1$

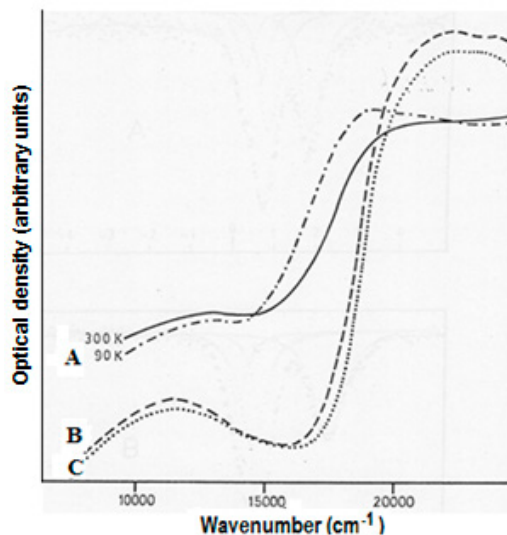
temperature the bulk  $[\text{Fe}(\text{pbo})_3](\text{BPh}_4)_2$  contains the low-spin species.

### 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  $20000 \text{ cm}^{-1}$  at room temperature to  $18000 \text{ cm}^{-1}$  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  $[\text{Fe}(\text{pbt})_3](\text{BPh}_4)_2$  [19] 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  $11500 \text{ cm}^{-1}$  (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  $22000 \text{ cm}^{-1}$ . The marked difference in

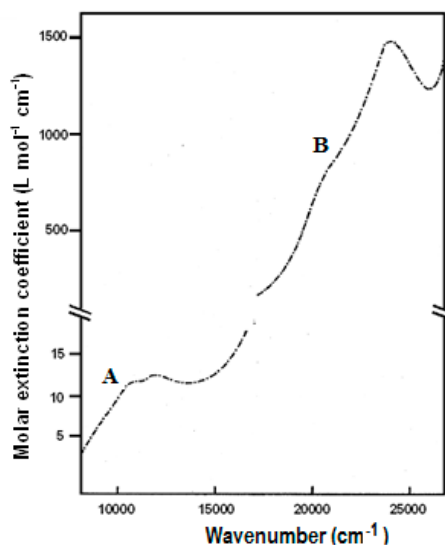


**Figure 5.** Diffuse reflectance spectra of A,  $[\text{}^{57}\text{Fe}(\text{pbo})_3](\text{BPh}_4)_2$ , B,  $[\text{Fe}(\text{pbo})_3](\text{BF}_4)_2$  and C,  $[\text{Fe}(\text{pbo})_3](\text{ClO}_4)_2$ .

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  $\text{cm}^{-1}$  ( $\epsilon = 11.5\text{-}12.5 \text{ L mol}^{-1} \text{ cm}^{-1}$ ). This band must arise from  ${}^5T_{2g} \rightarrow {}^5E_g$  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



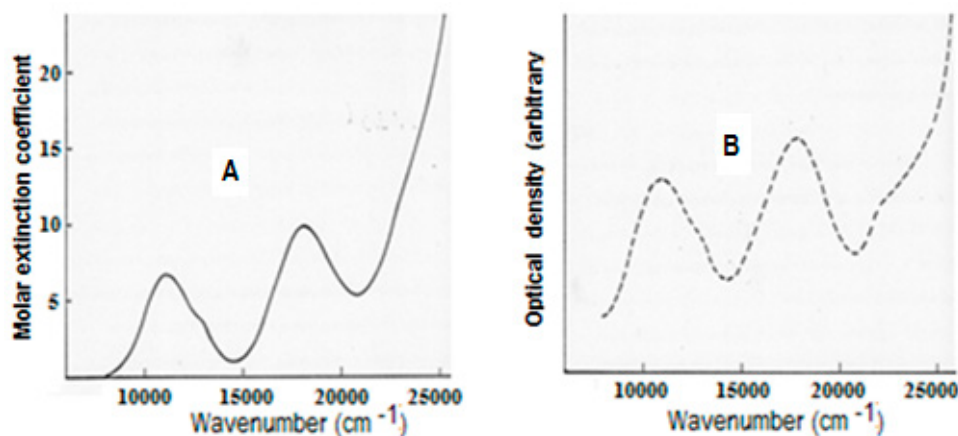
**Figure 6.** Electronic spectrum of  $[\text{Fe}(\text{pbo})_3](\text{BF}_4)_2$  in acetone solution,  $1.18 \times 10^{-3} \text{ M}$  (A) and  $10^{-2} \text{ M}$  (B).

of  $[\text{Fe}(pbo)_3]^{2+}$  shows a similar pattern to that of  $[\text{Fe}(pbt)_3]^{2+}$ , but a shoulder at about  $21000\text{cm}^{-1}$  ( $\epsilon = 850\text{ Lmol}^{-1}\text{cm}^{-1}$ ) appears more pronounced in the spectrum of the former. The charge transfer band is observed at about  $23500\text{ cm}^{-1}$  ( $\epsilon = 1450\text{ Lmol}^{-1}\text{cm}^{-1}$ ), significantly higher wavenumber than that for  $[\text{Fe}(pbt)_3]^{2+}$  (c.f. about  $19300\text{ cm}^{-1}$ ) 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  $[\text{Fe}(pbo)_3]^{2+}$  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,  $[\text{Ni}(pbo)_3](\text{ClO}_4)_2$ , 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  $11000\text{ cm}^{-1}$  ( $\epsilon = 6.8\text{ Lmol}^{-1}\text{cm}^{-1}$ ) and  $12600\text{ cm}^{-1}$  ( $\epsilon = 4.0\text{ Lmol}^{-1}\text{cm}^{-1}$ ), respectively. The second ligand field band,  ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ , occurs about  $18000\text{ cm}^{-1}$  leading to the ratio  $\nu_2 : \nu_1 = 1.64$



**Figure 7.** Electronic spectra of  $[\text{Ni}(pbo)_3](\text{ClO}_4)_2$  in acetonitrile solution ( $10^{-2}\text{ M}$ ), (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  $3.07\text{ BM}$  ( $\theta = -2\text{K}$ ) which indicates a slight orbital contribution arising from spin-orbit coupling. The ligand field strength ( $\nu_1$ ) observed for  $[\text{Ni}(pbo)_3]^{2+}$  here lies in the range originally predicted to encompass the value leading to the spin-crossover in the corresponding iron(II). In comparison to  $pbt$  (c.f.  $\nu_1 = 10800\text{ cm}^{-1}$ ,  $\epsilon = 11\text{ Lmol}^{-1}\text{cm}^{-1}$ , for  $[\text{Ni}(pbt)_3]^{2+}$  in aqueous acetone), the ligand field strength for  $pbo$  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  $[\text{Fe}(pbo)_3](X)_2$ , 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  $[\text{Fe}(\text{pbo})_3](\text{X})_2$  undergoes spin-state transition.

## REFERENCES

- [1] Gütlich P. and Goodwin H.A., *Spin Crossover in Transition Metal Compounds I*, Springer, Berlin, 2004.
- [2] Létard J.-F., Guionneau P. and Goux-Capes L., *Top. Curr. Chem.*, 2004; **235**: 221-249. DOI:10.1007/b95429.
- [3] Kahn O. and Codjovi E., *Philos. Trans. R. Soc. London, Ser. A*, 1996; **354(1706)**: 359-379. DOI:10.1098/rsta.1996.0012.
- [4] Khan O., Kröber J. and Jay C., *Adv. Mater.*, 1992; **4**: 718-728. DOI: org/10.1002/adma.19920041103.
- [5] Tao J., Wei R.-J., Huang R.-B., and Zheng L.-S., *Chem. Soc. Rev.*, 2012; **41**: 703-737. DOI: 10.1039/c1cs15136c.
- [6] Sugiyarto K.H. and Goodwin H.A., *Aust. J. Chem.*, 1988; **41**: 1645-63. DOI:10.1071/CH9881645.
- [7] Goodwin H.A. and Sugiyarto K.H., *Chem. Phys. Lett.*, 1987; **139**: 470-474. DOI: org/10.1016/0009-2614(87)80593-6.
- [8] Buchen T., Gütlich P. and Goodwin H.A., *Inorg. Chem.*, 1994; **33**: 4573-4576. DOI: 10.1021/ic00098a026.
- [9] Buchen T., Gütlich P., Sugiyarto K.H. and Goodwin H.A., *Chem. Eur. J.*, 1996; **2**: 1134-1138. DOI: org/10.1002/chem.19960020915.
- [10] König E., Kanellakopulos B., Powietzka B., and Goodwin H.A., *Inorg. Chem.*, 1989; **28**: 3993-3996. DOI: 10.1021/ic00320a011.
- [11] Sugiyarto K.H. and Goodwin, H.A., *Aust. J. Chem.*, 1994; **47**: 263-277. DOI: org/10.1071/CH9940263.
- [12] L. Lavrenova G., Shakirova O.G., Ikorskii V.N., Varnek V.A., Sheludyakova L.A., and Larionov S.V., *Russ. J. Coord. Chem.*, 2003; **29(1)**: 22-27. DOI: 10.1023/A:1021834715674.
- [13] Sugahara A., Kamebuchi H., Okazawa A., Enomoto M. and Kojima N., *Inorganics*, 2017; **5(3)**: 50. DOI:10.3390/inorganics5030050.
- [14] Attwood M., Akutsu H., Martin L., Cruickshank D., and Turner S.S., *Dalton Trans.*, 2019; **48**: 90-98; DOI: 10.1039/C8DT03240H.
- [15] McGarvey J.J., Lawthers I., Heremans K., and Toftlund H., *J. Chem. Soc., Chem. Commun.*, 1984; **23**: 1575-1576. DOI:10.1039/C39840001575.
- [16] Baker A.T. and Goodwin H.A., *Aust. J. Chem.*, 1977; **30**: 771-780, DOI: org/10.1071/CH9770771.
- [17] Sams J.R. and Tsin T.B., *J. Chem. Soc., Dalton Trans.*, 1976; **6**: 488-496. DOI:10.1039/DT9760000488.
- [18] Sams J.R. and Tsin T.B., *Inorg. Chem.*, 1976; **15(7)**: 1544-1550. DOI:10.1021/ic50161a016.
- [19] Baker A.T. and Goodwin H.A. *Aust. J. Chem.*, 1984; **37**: 1157-1162 DOI: org/10.1071/CH9841157.
- [20] Gan Q., Qi Y., Xiong Y., Fu Y. and Le X., *J. Fluoresc.*, 2016; **27(2)**: 1-14. DOI:10.1007/s10895-016-1999-5.
- [21] Chen Y.-L., Lee S.-W., Chi Y., Hwang K.-C., Kumar S.B., Hu Y.-H., Cheng Y.-M., Chou P.-T., Peng S.-M., Lee G.-H., Yeh S.-J. and Chen C.-T., *Inorg. Chem.*, 2005; **44(12)**: 4287-4294. DOI: 10.1021/ic050036y.
- [22] Hisano T., Ichikawa M., Tsumoto K. and Tasaki M., *Chem. Pharm. Bull.*, 1982; **30**: 2996-3004. DOI: org/10.1248/cpb.30.2996.

- [23] Figgis B.N. and Lewis J. in Lewis J. and Wilkins R.G. (Eds), *Modern Coordination Chemistry*, Interscience Publishers Inc., New York, 1960: 400-454. ISBN: 0470531967 9780470531969
- [24] Vogel A.I., *A Textbook of Qualitative Inorganic Analysis*, 5<sup>th</sup> Edn., Longman Inc, New York. 1979.
- [25] Cohen V.I., *J. Heterocycl. Chem.*, 1979; **16(1)**: 13-16. DOI: org/10.1002/jhet.5570160103.
- [26] Goodwin, H.A., *Coord. Chem. Rev.*, 1976; **18(3)**: 293-325. DOI: 10.1016/s0010-8545(00)80430-0.
- [27] Gütlich P., *Adv. Chem. Ser.*, 1981; **194**: 405-452. DOI: 10.1021/ba-1981-0194.ch019
- [28] Lever A.B.P., *Inorganic Electronic Spectroscopy*, Elsevier Publishing Company, Amsterdam. 1968.