

Six-Coordinate High-Spin Iron(II) Complexes with Bidentate PN Ligands Based on 2-Aminopyridine – New Fe(II) Spin Crossover Systems



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INTRODUCTION

In the quest for catalytically active non-precious metal systems many efforts are made to obtain hemilabile systems, which display enhanced reactivity through the accessibility of vacant coordination sites. During our investigations on Fe(II) systems with heterodifunctional PN-ligands, based on 2-aminopyridine, we obtained several novel octahedral iron(II) complexes of the type $[\text{Fe}(\text{PN}^{\text{R}}\text{-Ph})_2\text{X}_2]$ ($\text{X} = \text{Cl}, \text{Br}; \text{R} = \text{H}, \text{Me}$).^[1]

The use of these similar ligands, N-diphenylphosphino-2-aminopyridine ($\text{PN}^{\text{H}}\text{-Ph}$) and its N-methylated derivative ($\text{PN}^{\text{Me}}\text{-Ph}$), led to compounds with comparable geometry, but strikingly different properties, chemical behavior and isomerism.

This influence of the N-methylation is also a driving force for the Fe(II)-spin state. For $[\text{Fe}(\text{PN}^{\text{Me}}\text{-Ph})_2\text{X}_2]$ ($\text{X} = \text{Cl}, \text{Br}$) the high-spin state is temperature independent, whereas the series of $[\text{Fe}(\text{PN}^{\text{H}}\text{-Ph})_2\text{X}_2]$ ($\text{X} = \text{Cl}, \text{Br}$) contributes to the rare class of octahedral Fe(II) complexes with phosphine ligands undergoing an S=2 to S=0 spin crossover at low temperatures.

Isomerism of $[\text{Fe}(\text{PN}^{\text{R}}\text{-Ph})_2\text{X}_2]$

For octahedral complexes of the general formula $[\text{Fe}(\text{PN}^{\text{R}}\text{-Ph})_2\text{X}_2]$ principally five isomeric coordination patterns are possible.

For the methylated derivatives $[\text{Fe}(\text{PN}^{\text{Me}}\text{-Ph})_2\text{X}_2]$ only a single isomer, having all donor atoms of the $\text{PN}^{\text{Me}}\text{-Ph}$ ligands *trans* to one another, is found. This was confirmed by single-crystal X-Ray analysis. (Fig.1)

For the $[\text{Fe}(\text{PN}^{\text{H}}\text{-Ph})_2\text{X}_2]$ system the 'PN-ligands most likely exhibit a *cis*-Cl,P,N-arrangement. This was confirmed by theoretical calculations, (Fig.2) as well as by a detailed IR-spectroscopic study.

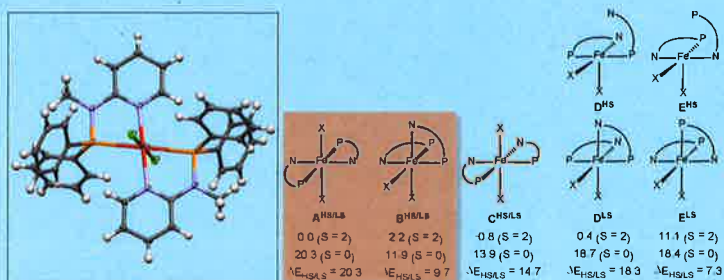


Fig. 1 Molecular structure of all-*trans*-Cl,P,N-[Fe(PN^H-Ph)₂Cl] Fig. 2 Different isomers and calculated energies for [Fe(PN^H-Ph)₂X₂]

Spin Crossover of $[\text{Fe}(\text{PN}^{\text{H}}\text{-Ph})_2\text{X}_2]$

$[\text{Fe}(\text{PN}^{\text{H}}\text{-Ph})_2\text{X}_2]$ contributes to the rare class of octahedral Fe(II) complexes with phosphine ligands undergoing an S=2 to S=0 spin crossover at low temperatures. The spin transition was monitored by SQUID (Fig.3) and ⁵⁷Fe-Mössbauer-spectroscopy, (Fig.4) as well as by temperature dependent IR-spectroscopy.

The fact that all other investigated compounds do not show a thermal spin transition, can be seen as additional hint for the significantly different molecular structure of $[\text{Fe}(\text{PN}^{\text{H}}\text{-Ph})_2\text{X}_2]$.

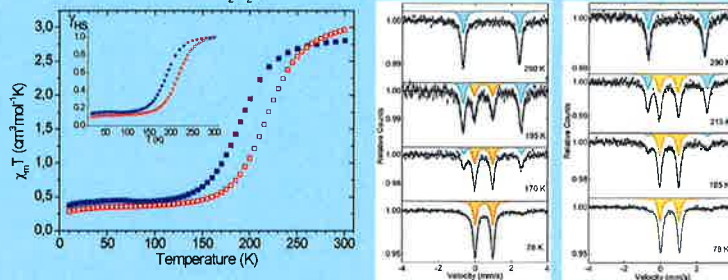


Fig. 3 Magnetic behaviour of [Fe(PN^H-Ph)₂Cl] (blue) and [Fe(PN^H-Ph)₂Br] (red) Fig. 4 ⁵⁷Fe-Mössbauer of [Fe(PN^H-Ph)₂Cl] (left) and [Fe(PN^H-Ph)₂Br] (right)

Isomeric assignment via FIR spectroscopy

Due to the intrinsic insolubility of $[\text{Fe}(\text{PN}^{\text{H}}\text{-Ph})_2\text{X}_2]$ and therefore lacking crystallographic characterization, the molecular structure was assigned by alternative techniques. Due to the different vibrational modes expected for the theoretically possible isomers, in a dual experimental and theoretical approach it was possible to identify the *cis*-Cl,P,N- geometry for the investigated compounds.

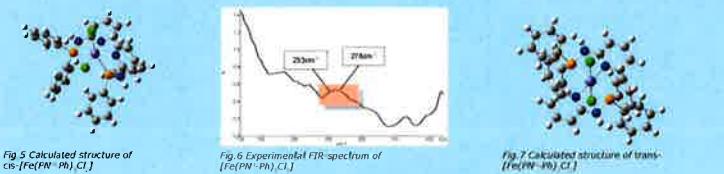


Fig. 5 Calculated structure of *cis*-[Fe(PN^H-Ph)₂Cl] Fig. 6 Experimental FIR spectrum of *cis*-[Fe(PN^H-Ph)₂Cl] Fig. 7 Calculated structure of *trans*-[Fe(PN^H-Ph)₂Cl]

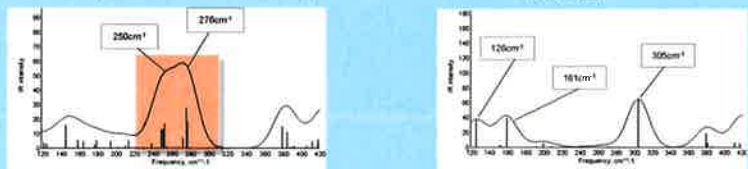


Fig. 8 Calculated FIR spectrum of *cis*-[Fe(PN^H-Ph)₂Cl] Fig. 9 Calculated FIR spectrum of *trans*-[Fe(PN^H-Ph)₂Cl]

CONCLUSION

- Novel Fe(II)-complexes with hemilabile PN-ligands were prepared and characterized by various methods.
- The use of two similar ligands ($\text{PN}^{\text{R}}\text{-Ph}$, R= H, Me) yields isomeric structures, differing in reactivity, properties and stability.
- Temperature dependent MIR/FIR spectroscopy was successfully applied in detecting and monitoring the spin state and isomeric assignment.
- Depending on the solvent, $[\text{Fe}(\text{PN}^{\text{H}}\text{-Ph})_2\text{X}_2]$ reveals variable reactivity, allowing for further reactions.

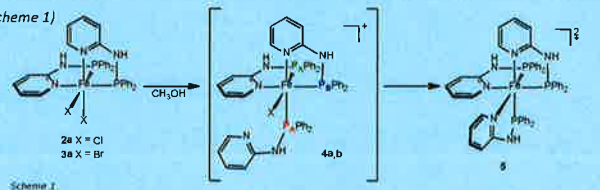
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[1] C. Holzhaecker, M. J. Calhorda, A. Gil, M. D. Carvalho, L. P. Ferreira, B. Stoeger, K. Mereiter, M. Weil, D. Mueller, P. Weinberger, E. Pittenauer, G. Allmaier, K. Kirchner, Dalton Trans., 2014, in press. [2] Gaussian 09, Revision C.01. M. J. Frisch et al. Gaussian, Inc. Wallingford CT, 2010.

Rearrangement reactions

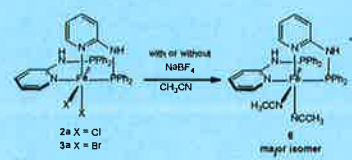
In order to get further insights in the reactivity of the $[\text{Fe}(\text{PN}^{\text{H}}\text{-Ph})_2\text{X}_2]$ family, several experiments regarding possible rearrangement and redistribution reactions were performed.

In MeOH $[\text{Fe}(\text{PN}^{\text{H}}\text{-Ph})_2\text{X}_2]$ is substitutionally labile. Through a κ^1 -coordinated intermediate a dicationic tris- $\text{PN}^{\text{H}}\text{-Ph}$ complex with a tetrahaloferrate anion is obtained. (Scheme 1)



Scheme 1

In comparison, in acetonitrile solution only the two coordinated halogens are exchanged by an acetonitril ligand. Addition of NaBF_4 as halogen scavenger has no further influence. (Scheme 2)



Scheme 2