Hyperfine Interactions (2021) 242: 8
https://doi.org/10.1007/s10751-021-01730-w

Pyrazole's substituents effect on the spin state of $[Fe(bpp)_2]^{2+}$complexes

Afaf Oulmidi[1,2] · Aurelian Rotaru[3] · Smaail Radi[1] · Yann Garcia[2]

Accepted: 20 September 2021/ Published online: 13 October 2021
© The Author(s), under exclusive licence to Springer Nature Switzerland AG 2021

Abstract
2,6-dipyrazolyl pyridine (bpp) skeleton is a good building unit for iron(II) spin crossover research. Various functional groups can be appended on pyrazolyl and pyridine rings thereby modifying potentially the spin state properties of $[Fe(bpp)_2]^{2+}$ derivatives. In this work, we have worked on substituted pyrazole by grafting an ester function as an electro-attractor group and a methyl substituent as an electro-donating group in 3 and 5 positions, respectively. Mössbauer analyses of the mononuclear complex **1** $[FeL_2](ClO_4)_2$ (***L***= diethyl-1,1'-(pyridine-2,6-diyl)bis(5-methyl-1H-pyrazole-3-carboxylate) revealed high-spin iron(II) ions at room temperature. On cooling down to liquid helium temperature, magnetic susceptibility measurements confirmed a paramagnetic state, suggesting that the steric influence of the pyrazole substituents was to great to allow a thermally induced spin crossover to occur.

Keywords Iron(II) complexes · bpp ligand · ^{57}Fe Mössbauer spectroscopy · spin crossover

1 Introduction

Pyridine and its derivatives form one of the most widely studied classes of ligands in coordination chemistry, in particular terpyridine, in iron chemistry. Their popularity is due to synthetic accessibility of substituted terpyridines and their ability to generate remarkable

This article is part of the Topical Collection on *Proceedings of the International Conference on the Applications of the Mössbauer Effect (ICAME 2021), 5-10 September 2021, Brasov, Romania*
Edited by Victor Kuncser

✉ Yann Garcia
yann.garcia@uclouvain.be

[1] LCAE, Department of Chemistry, Faculty of Sciences, University Mohamed I, 524, 60 000 Oujda, BP, Morocco

[2] Institute of Condensed Matter and Nanosciences, Molecular Chemistry, Materials and Catalysis (IMCN), Université catholique de Louvain, Place L. Pasteur 1, 1348 Louvain-la-Neuve, Belgium

[3] Department of Electrical Engineering and Computer Science & Research Center MANSiD, "Stefan cel Mare" University, University Street, No. 13, 720229 Suceava, Romania

properties including redox or spin crossover (SCO) phenomena [1,2,3] However, the combination of pyridyl functional group and other *N*-donors aromatic group in one organic ligand may lead to intriguing structural motifs. Therefore, other classes of *NNN* tridentate ligands such as 2,6-di(benzimidazol-2-yl)pyridines [4] and 2,6-di(pyrazolyl)pyridines [5,6] have been developed. Based on the above ideas, we pre-selected 2,6-bis(pyrazolyl)pyridine (1-bbp) as ligand. The particularity of this skeleton is its ability to be substituted at every position on both pyrazole and pyridine rings [5]. Substitution at pyrazole groups provides steric and electronic control of the metal centre. While adding functional groups on pyridine ring allows the introduction of functional groups at the periphery of the complex without affecting the metal center [7]. This flexibility had led bpp iron complexes to be included in a variety of multifunctional SCO molecular switches [8], magnetic materials [9] and so on.

In this work, we present another 2,6-di(pyrazolyl)pyridine derivative by introducing attractor and donor groups in 3 and 5 positions of a pyrazole ring, respectively. We discuss the Mössbauer and magnetic investigation of the obtained mononuclear iron complex.

2 Experimental

The ligand diethyl-1,1'-(pyridine-2,6-diyl)bis(5-methyl-1H-pyrazole-3-carboxylate) ***L***, was prepared by nucleophilic aromatic substitution reaction of pyrazolic anions with 2,6-dibromopyridine [10]. Complex $[FeL_2](ClO_4)_2$ (**1**) was prepared as follows: to a solution of ***L*** (38.3 mg, 0.1 mmol) in chloroform (20 mL) wad added a solution of $Fe(ClO_4)_2 \cdot 6H_2O$ (18.1 mg, 0.05 mmol) in acetone (10 mL) and the mixture was stirred for 15 min. An orange/yellow solution was formed. A solution of diethyl ether (40 mL) was then added dropwise to the solution causing an immediate yellow precipitate. After the solution was stirred for 30min at room temperature, the yellow precipitate was collected and washed with diethyl ether. Recrystallisation was carried out by dissolving the precipitate in nitromethane (6 mL) and vapour diffused with Et_2O over two weeks. Yellow crystals were collected by filtration. Yield 31% (16 mg). FT-IR/cm^{-1} 3134 (w), 2994 (w), 1635 (m), 1235 (s), 856 (w). HRMS (ESI): m/z: 921.2016 [$2M^{35}ClO_4{}^{56}Fe$].

All solvents and chemicals were obtained from commercial sources and used without purification.^{57}Fe Mössbauer spectra were recorded in transmission geometry with a constant acceleration mode conventional WissEl GmbH spectrometer equipped with a 50 mCi ^{57}Co(Rh) source and a Reuter Stokes proportional counter. The powdered samples were sealed in aluminium foil and spectra were recorded at 298 K. Spectra were fitted using Recoil 1.05 Mössbauer Analysis software [11]. Isomer shift values are given with respect to α-Fe at 298 K. Magnetic susceptibilities were measured on a Quantum design MPMS-5s SQUID magnetometer. The magnetic data were corrected for the sample holder and diamagnetic contributions. The polycrystalline sample was quickly loaded into a gelatine capsule and immediately inserted within the SQUID cavity.

3 Results and discussion

^{57}Fe Mössbauer spectra of **1** before (Figure 1) and after recrystallization (Figure 2) have been recorded at room temperature. Related parameters are gathered in Table 1. At 298 K, the

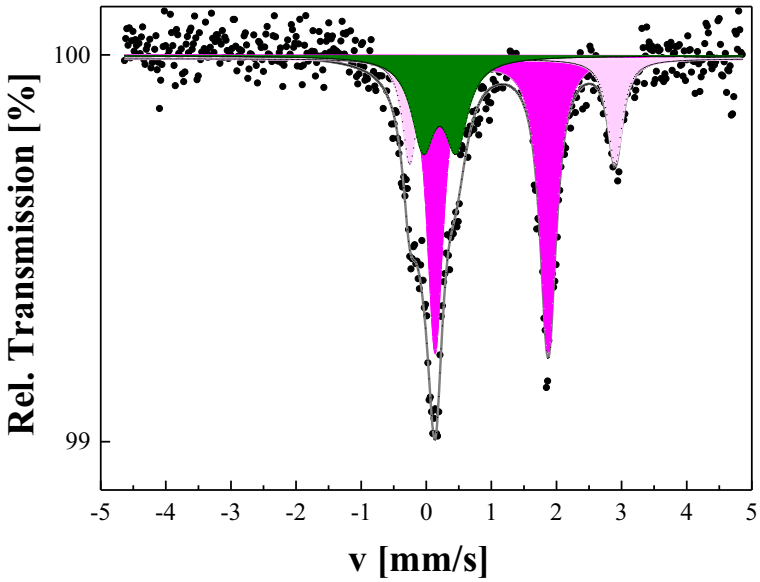


Fig. 1 ^{57}Fe Mössbauer spectrum of the precipitate of **1** recorded at room temperature. Purple, pink and green quadrupole doublets correspond to HS Fe(II) and Fe(III) ions, respectively

spectrum of the precipitate shows a major quadrupole doublet with an isomer shift $\delta = 1.00(1)$ mm s^{-1} and a quadrupole splitting $\Delta E_Q = 1.73(1)$ mm s^{-1} diagnostic of Fe(II) ions in the high-spin (HS) state (Figure 1). Such parameters are similar to those observed in other Fe(II) complexes with *NNN* tridentate ligands with narrow bites like bpp ligand [12,13]. An additional symmetrical doublet characterized by $\delta = 1.32(1)$ mms^{-1} with a large $\Delta E_Q =$

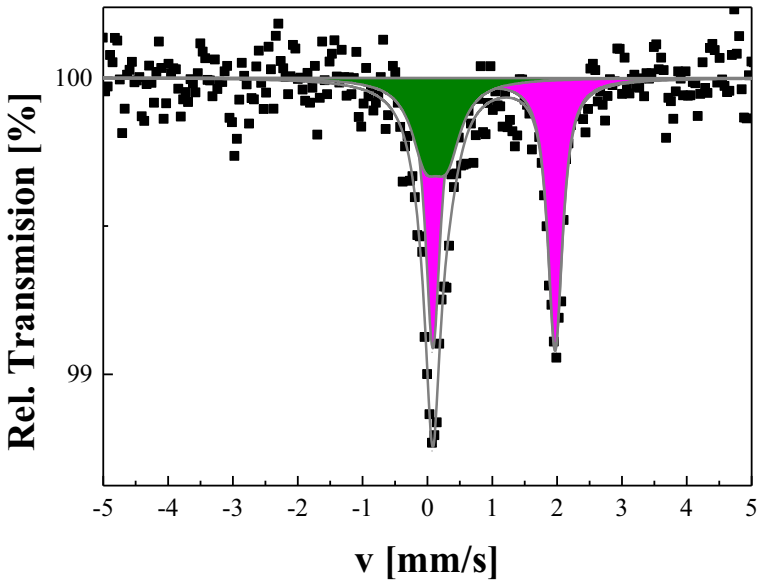


Fig. 2 ^{57}Fe Mössbauer spectrum of single crystals of **1** at room temperature

Table 1 Overview of ^{57}Fe Mössbauer parameters for **1** for spectra recorded at room temperature

Sample	Spin State	A/A_{tot}	Mössbauer parameters		
			δ (mm s^{-1})	ΔE_Q (mm s^{-1})	$\Gamma/2$
1 powder	HS Fe(II)	58	1.00(1)	1.73(1)	0.14(1)
	$[Fe(ClO_4)_2]\cdot 6H_2O$	18	1.32(1)	3.15(3)	0.13(3)
	HS Fe(III)	24	0.20(3)	0.51(1)	0.21(5)
1 crystals	HS Fe(II)	67	1.02(1)	1.88(3)	0.13(2)
	HS Fe(III)	33	0.14(1)	0.33(2)	0.26(1)

δ: isomer shift (with respect to α-Fe at 298 K); ΔE_Q: quadrupole splitting; $\Gamma/2$: half width at half maximum

3.15(3) mm s^{-1} is also present arising from the perchlorate Fe(II) salt used in the preparation of **1**, $[Fe(ClO_4)_2]\cdot 6H_2O$, as found in an earlier literature report, after the deposition of this salt on a bio-membrane (δ = 1.34(2) mms^{-1}) [14]. Apart from this, we also notice a third contribution due to Fe(III) ions in the HS state, with δ = 0.20(3) mm s^{-1} and ΔE_Q = 0.51(1) mm s^{-1}, which is in good agreement with previous reported values [14].

After recrystallisation, a Mössbauer analysis revealed a quadrupole doublet with δ = 1.02(1) mm s^{-1} and ΔE_Q = 1.88(3) mm s^{-1} indicative of HS Fe(II) ions (Figure 2). The observed asymmetry of the lines is due to a texture effect. This experiments thus confirms the success of the recrystallisation with the disappearance of the signal associated to $[Fe(ClO_4)_2]\cdot 6H_2O$. Long acquisition time afforded a second quadrupole doublet with δ = 0.14(1) mm s^{-1} and ΔE_Q = 0.33(2) mm s^{-1}, characteristic of HS Fe(III) ions [15].

The solid-state magnetic behavior of **1** was investigated by variable-temperature magnetic susceptibility measurements over the range 300-4 K (Figure 3) on fresh crystals to track any possible spin state crossover. A constant $\chi_M T$ value of 3.7(1) cm^3 K mol^{-1} , indicative of HS Fe(II) ions, was observed over the whole temperature range investigated, thus confirming a paramagnetic behavior. This result is consistent with a rigid solid lattice which prevents any

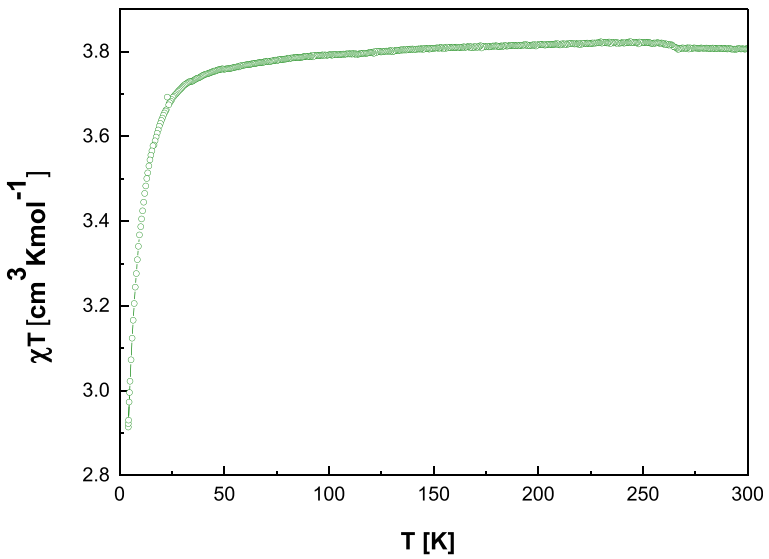


Fig. 3 Temperature-dependent $\chi_M T$ plot for single crystals of **1** over the range 300-4 K

spin state crossover to occur on this material [16]. The drop of the $\chi_M T$ value below 25 K is due to zero-field splitting of HS Fe(II) ions.

4 Conclusions

Insertion of substituents on the bispyrazolyl pyridine bpp skeleton is believed to influence strongly the properties of $[Fe(bpp)_2]^{2+}$ complexes, in particularly spin crossover properties. In this work, we show that the introduction of both ester and methyl groups into 3,5 positions on pyrazole ring respectively trap the Fe(II) center in its high-spin state, preventing it to be converted to the low-spin state at all temperatures. Steric and electronic properties of substituents need to be taken into account.

Acknowledgements This research was supported by a bilateral WBI-Morocco grant (COP 22 Program 2018–2022), the Fonds de La Recherche Scientifique—FNRS (CDR 33694457, PDR T.0095.21), PPR2-MESRSFC-CNRST-P10 project (Morocco), CCCDI - UEFISCDI, project number PN-III-CEI-BIM-PBE-2020-0042/8 BM / 2021, Ministère de l'Education et de la Recherche de Roumanie and WBI. We thank CNRST Morocco and WBI-Morocco for an excellence PhD stipendium, UCLouvain international action committee for a PhD scholarship allocated to A.O and GFSM for supporting participation of A.O to ICAME 2021.

References

1. Wild, A., Winter, A., Schlütter, F., Schubert, U.S.: Advances in the field of π-conjugated 2,2:6,2″-terpyridines. Chem. Soc. Rev. **40**, 1459 (2011)
2. Shunmugam, R., Gabriel, G.J., Aamer, K.A., Tew, G.N.: Metal–Ligand-Containing Polymers: Terpyridine as the Supramolecular Unit. Macromol. Rapid Commun. **31**, 784–793 (2010)
3. Nishihara, H., Kanaizuka, K., Nishimori, Y., Yamanoi, Y.: Construction of redox- and photo-functional molecular systems on electrode surface for application to molecular devices. Coord. Chem. Rev. **251**, 2674–2687 (2007)
4. Boca, M., Jameson, R.F., Linert, W.: Fascinating variability in the chemistry and properties of 2,6-bis-(benzimidazol-2-yl)-pyridine and 2,6-bis-(benzthiazol-2-yl)-pyridine and their complexes. Coord. Chem. Rev. **255**, 290–317 (2011)
5. Halcrow, M.A.: Iron(II) complexes of 2,6-di(pyrazol-1-yl)pyridines—A versatile system for spin-crossover research. Coord. Chem. Rev. **253**, 2493–2514 (2009)
6. Kershaw Cook, L.J., Mohammed, R., Sherborne, G., Roberts, T.D., Alvarez, S., Halcrow, M.A.: Spin state behaviour of iron(II)/dipyrazolylpyridine complexes. New insights from crystallographic and solution measurements. Coord. Chem. Rev. **289–290**, 2–12 (2015)
7. Roberts, T.D., Halcrow, M.A.: Polyhedron. **64**, 4–12 (2013)
8. Olguin, J., Brooker, D.S.: Spin crossover active iron(II) complexes of selected pyrazole pyridine / pyrazine ligands. Coord. Chem. Rev. **255**, 203–240 (2011)
9. Abhervé, A., Recio-Carretero, M.J., López-Jordà, M., Clemente-Juan, J.M., Canet-Ferrer, J., Cantarero, A., Clemente-León, M., Coronado, E.: Nonanuclear spin-crossover complex containing iron(II) and iron(III) based on a 2,6-bis(pyrazol-1-yl)pyridine ligand functionalized with a carboxylate group. Inorg. Chem. **55**, 9361–9367 (2016)
10. Oulmidi, A., Radi S., Idir A., Zyad A., Kabach I., Nhiri M., Robeyns K., Rotaru A., Garcia Y., Synthesis and Cytotoxicity against Tumor Cells of Pincer N-heterocyclic Ligands and their Transition Metal complexes , RSC Adv (2021, submitted).
11. Lagarec, K., Rancourt, D. G. Recoil, Mössbauer Spectral Analysis software for Windows 1.0; Department of Physics, University of Ottawa Ottawa, ON (1998)
12. Kulmaczewski, R., Shepherd, H.J., Cespedes, O., Halcrow, M.A.: A Homologous Series of $[Fe(H_2Bpz_2)_2(L)]$ Spin-Crossover Complexes with Annelated Bipyridyl Co-Ligands. Inorg. Chem. **53**(18), 9809–9817 (2014)

13. Halcrow, M.A.: The synthesis and coordination chemistry of 2,6-bis(pyrazolyl)pyridines and related ligands — Versatile terpyridine analogues. Coord. Chem. Rev. **249**, 2880 (2005)
14. Naik, A.D., Garcia, Y.: ^{57}Fe Mössbauer probe of spin crossover thin films on a bio-membrane. Hyperfine Interact. **206**, 7–11 (2012)
15. Naik, A.D., Dîrtu, M.M., Garcia, Y.: Neutral and anionic duality of 1,2,4-triazole α-amino acid scaffold in 1D coordination polymers. Hyperfine Interact. **205**, 57–61 (2012)
16. Roberts, T.D., Little, M.A., Kershaw Cook, L.J., Barrett, S.A., Tuna, F., Halcrow, M.A.: Iron(II) complexes of 2,6-di(1-alkylpyrazol-3-yl)pyridine derivatives – The influence of distal substituents on the spin state of the iron centre. Polyhedron. **64**, 4–12 (2013)

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.