Hyperfine Interactions (2019) 240: 91
https://doi.org/10.1007/s10751-019-1638-z

Ligand field strength tuning in the model $[Fe(H_2Bpz_2)_2(bipy)]$ spin crossover complex

Shufang Xue[1] · **Aurelian Rotaru**[2] · **Yann Garcia**[1]

Abstract

The original magnetism of a model spin crossover complex $[Fe(H_2Bpz_2)_2(bipy)]$ (H_2Bpz_2 = dihydrobis(1-pyrazolyl)borate, bipy = 2,2′-bipyridine) has been altered from spin state switching to paramagnetic behavior, through grafting a weak electronic-donating group: bromomethyl (in **1**) and Br (in **2**) onto the bipy ligand at positions C5 and C5′. The introduction of the electron-donating bromo groups into the bipy ligand reduce the π-acceptor character, leading to a weaker ligand field strength, thus stabilizing the high-spin state.

Keywords Iron(II) complexes · Spin crossover · ^{57}Fe Mossbauer spectroscopy

1 Introduction

Iron(II) spin crossover (SCO) materials have been widely studied as molecular switches with a wide variety of potential applications, including displays, sensors, actuators or memory components [1]. The properties referring to high transition temperature ($T_{1/2}$), abruptness [2] and hysteresis [3] are largely a product of fine-tuning the interaction between the Fe^{II} ion and the ligand field as well as supramolecular interactions in the crystal lattice. Complexes derived from the parent complex $[Fe(H_2Bpz_2)_2(bipy)]$ (pz = pyrazolyl; bipy = bipyridine) [4] can be high-spin (HS) [5] or SCO active [5–11] depending on the ligand substituents. In essence, the

---

This article is part of the Topical Collection on *Proceedings of the 5th Mediterranean Conference on the Applications of the Mössbauer Effect (MECAME 2019) and 41st Workshop of the French-speaking Group of Mössbauer Spectroscopy (GFSM 2019), Montpellier, France, 19-23 May 2019*
Edited by Pierre-Emmanuel Lippens, Yann Garcia, Moulay-Tahar Sougrati and Mira Ristic (†)

✉ Yann Garcia
yann.garcia@uclouvain.be

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

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

spin nature of these complexes lies in the high σ-donor power of the imine function and the empty, low-lying π orbitals of the ligand molecules. Therefore, an effective strategy for tuning the ligand field strength of bipy complexes into the crossover range consists of modifying the σ-donor or π-acceptor character of the ligand molecules. Our laboratory is currently undergoing a systematic study to investigate electronic effects on SCO Fe^{II} complexes in which donor and acceptor groups are varied at the 5 and 5'positions on the bipy ligand. Herein, we present another two bipy-related ligands by introcution of halogen atoms or weak eletron-donating groups and self-assembly of the novel iron-bipy systems (Fig. 1), where magnetic measurements revealed that both of them exhibit on cooling from room temperature to liquid helium temperature, characteristic paramagnetic behavior.

2 Experimental

The ligands 5,5′-bis(bromomethyl)-2,2′-bipyridine (bipy-CH$_2$Br) [12] and 5,5′-dibromo-2,2′-bipyridine (bipy-Br) [13] were synthesized following a reported procedure. Complex **1** was prepared as follows: to a solution of K[H$_2$B(pz)$_2$] (44 mg, 0.24 mmol) in methanol (2 mL) was added a solution of Fe(ClO$_4$)$_2$·6H$_2$O (44 mg, 0.12 mmol) in methanol (2 mL). The formed KClO$_4$ precipitate was removed by filtration, affording a yellow solution. A solution of bipy-CH$_2$Br (34.2 mg, 0.1 mmol) in dichloromethane (2 mL) was then added dropwise to the solution, causing an immediate color change to brown. After the solution was stirred for 2 h at room temperature, the brown precipitate was collected, washed with methanol, and dried under a stream of N$_2$(g). Yield: 41 mg (59%). Anal. Calcd. for **1** ($C_{24}H_{26}B_2Br_2N_{10}Fe$): C, 41.67; H, 3.79; N, 20.25. Found: C, 41.15; H, 3.64; N, 20.01. MS (FTMS + pESI): m/z 692.02 [M+]. For **2**, the same method that was used for **1** was followed using bipy-Br (31.3 mg, 0.1 mmol) in 2 mL THF, which yielded a cyan precipitate. Yield: 30 mg (45%). Anal. Calcd. for **2** ($C_{22}H_{22}B_2Br_2N_{10}Fe$): C, 39.81; H, 3.34; N, 21.10. Found: C, 39.42; H, 3.29; N, 20.92. MS (FTMS + pESI): m/z 663.99 [M+].

Elemental analyses for C, H and N were performed at Medac. Mass spectra (MS) were recorded using a Q-Exactive ThermoFisher spectrometer. Magnetic susceptibilities were measured on a Quantum design MPMS-5 s 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. ^{57}Fe Mössbauer spectra were recorded in transmission geometry with a constant acceleration mode conventional spectrometer equipped with a 50 mCi ^{57}Co(Rh) source and a Reuter Stokes

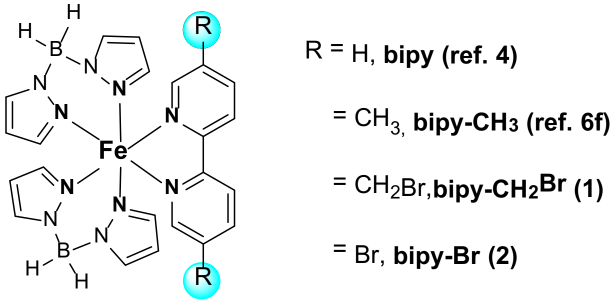

Fig. 1 Schematic representation of Fe^{II} complexes based on two substituted bipy ligands at positions C5 and C5′

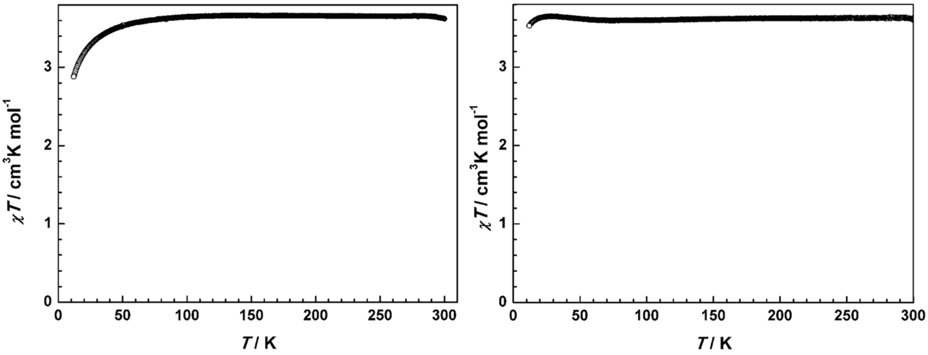

Fig. 2 Temperature-dependent $\chi_M T$ plot for complexes **1** (left) and **2** (right)

proportional counter. The powdered samples were sealed in aluminium foil and spectra were recorded at 298 K. The spectra were fitted using Recoil 1.05 Mössbauer Analysis software [14]. The isomer shift values are given with respect to α-Fe at 298 K.

3 Results and discussion

The solid-state magnetic behavior of both complexes was probed by variable-temperature direct current (dc) susceptibility measurements over the range 300–12 K on polycrystalline samples under an applied field of 1 T (Fig. 2). Complex **1** exhibits characteristic paramagnetic behavior over the entire temperature range, with a constant $\chi_M T$ value of 3.6 cm^3 mol^{-1} K at 300 K, the value being in good agreement with pure non-interacting HS Fe^{II} species. Note that the gradual decrease of the $\chi_M T$ value below 50 K could be due to weak intermolecular antiferromagnetic interactions and/or zero-field splitting of Fe(II) ions. In contrast, $\chi_M T$ value of **2** keeps constant over the temperature range at 3.6 cm^3 mol^{-1} K. Those above analysis indicate that the introduction of the electron-donating bromomethyl or bromo groups onto the bipy backbone cripple the ability of π-electron acceptor, thus stabilizing the HS state.

^{57}Fe Mössbauer spectroscopy of **1** and **2** was applied to investigate the stability of our materials (iron oxidation) and to determine the spin states nature of these materials (Fig. 3 and Table 1). As shown in Table 1, **1** displays an isomer shift (δ) of 1 mm s^{-1} at room temperature.

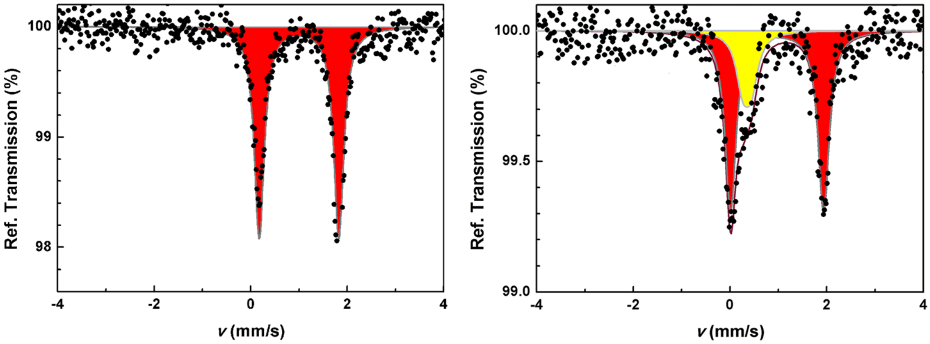

Fig. 3 ^{57}Fe Mössbauer spectra of polycrystalline samples for complexes **1** (left) and **2** (right) recorded at 298 K. Red and yellow correspond to the Fe^{II} HS and Fe^{III} impurity, respectively

Table 1 Overview of selected ^{57}Fe Mössbauer parameters for 1 and 2

Complex	T / K	A_{HS}/A_{tot}(%)	HS Fe^{II} (mm/s)			Fe^{III} (mm/s)		
			δ	ΔE_Q	$\Gamma/2$	δ	ΔE_Q	$\Gamma/2$
1	298(1)	100	1.00(1)	1.65(1)	0.13(8)	–	–	–
2	298(1)	75.7(9)	0.98(1)	1.92(3)	0.14(2)	0.35(5)	0.18(1)	0.16(1)

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

An identical room temperature δ was found for the mononuclear SCO complex $[Fe(H_2Bpz_2)_2(EtObpydc)]$ (EtObpydc = diethyl-2,2′-bipyridyl-5,5′-dicarboxylate)[6f]. Similar isomer shift as for **2** was found at room temperature for the SCO mononuclear $[Fe(H_2Bpz_2)_2(i\text{-}PrObpydc)]$ (i-PrObpydc = diisopropyl-2,2′-bipyridyl-5,5′-dicarboxylate)[6f]. These result unambiguously confirm that the coordination sphere made HS $Fe^{II}N_6$ species made of two hydrobis(1-pyrazolyl)borate and one 2,2′-bipyridine ligands is confirmed. For **2**, Fe(III) species reflected by an isomer shift (δ) of 0.35 mm s^{-1} are revealed at room temperature as observed in $[Fe(H_2Bpz_2)_2(i\text{-}PrObpydc)]$.[6f] (Fig. 3), presumably due to air oxidation.

4 Conclusions

The foregoing results demonstrate that the introduction of the electron-donating bromomethyl groups or halogen group into the bipy ligand can reduce the π-acceptor character leading to a weaker ligand field strength and stabilizing the HS state in $[Fe(H_2Bpz_2)_2(bipy\text{-}type)]$. Such compounds are potential switches under an applied pressure, which makes them attractive as pressure spin crossover sensors [15, 16]. Further studies on the decoration of electron-withdrawing substituents presenting abrupt and hysteretic spin crossover behaviors centered near room temperature are currently underway in our laboratory.

Acknowledgements We acknowledge support from the Fonds National de la Recherche Scientifique-FNRS (PDR T.0102.15, CDR 33694457), the Romanian National Authority for Scientific Research, CNCSUEFISCDI, Project PN-II-RU-TE-2014-4-2695, FNRS-Academie Roumaine, WBI Roumanie, and COST Action CA15128. We thank GFSM for supporting attendance of S. Xue to GFSM 2019 (Montpellier).

References

1. Gütlich, P., Gaspar, A.B., Garcia, Y.: Spin state switching in iron coordination compounds. Beilstein J. Org. Chem. **9**, 342 (2013)
2. Dîrtu, M.M., Neuhausen, C., Naik, A.D., Rotaru, A., Spinu, L., Garcia, Y.: Insights into the origin of cooperative effects in the spin transition of $[Fe(NH_2trz)_3](NO_3)_2$: the role of supramolecular interactions evidenced in the crystal structure of $[Cu(NH_2trz)_3](NO_3)_2{\cdot}H_2O$. Inorg. Chem. **49**, 5723 (2010)
3. Dîrtu, M.M., Naik, A.D., Rotaru, A., Spinu, L., Poelman, D., Garcia, Y.: Fe^{II} spin transition materials including an amino–Ester 1,2,4-Triazole derivative, operating at, below, and above room temperature. Inorg. Chem. **55**, 4278 (2016)
4. Real, J.A., Muñoz, M.C., Faus, J., Solans, X.: Spin crossover in novel Dihydrobis(1-pyrazolyl)borate $[H_2B(pz)_2]$-containing Iron(II) complexes. Synthesis, X-ray structure, and magnetic properties of $[FeL\{H_2B(pz)_2\}_2]$ (L = 1,10-Phenanthroline and 2,2‘-Bipyridine). Inorg. Chem. **36**, 3008 (1997)
5. Luo, Y.-H., Nihei, M., Wen, G.-J., Sun, B.-W., Oshio, H.: Ambient-temperature spin-state switching achieved by protonation of the amino group in $[Fe(H_2Bpz_2)_2(bipy\text{-}NH_2)]$. Inorg. Chem. **55**, 8147 (2016)

6. Milek, M., Heinemann, F.W., Khusniyarov, M.M.: Spin crossover meets Diarylethenes: efficient Photoswitching of magnetic properties in solution at room temperature. Inorg. Chem. **52**, 11585 (2013)
7. 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**, 9809 (2014)
8. Luo, Y.-H., Liu, Q.-L., Yang, L.-J., Sun, Y., Wang, J.-W., You, C.-Q., Sun, B.-W.: Magnetic observation of above room-temperature spin transition in vesicular nano-spheres. J. Mater. Chem. C. **4**, 8061 (2016)
9. Moertel, M., Witt, A., Heinemann, F.W., Bochmann, S., Bachmann, J., Khusniyarov, M.M.: Synthesis, characterization, and properties of Iron(II) spin-crossover molecular Photoswitches functioning at room temperature. Inorg. Chem. **56**, 13174 (2017)
10. Kumar, K.S., Studniarek, M., Heinrich, B., Arabski, J., Schmerber, G., Bowen, M., Boukari, S., Beaurepaire, E., Dreiser, J., Ruben, M.: Engineering on-surface spin crossover: spin-state switching in a self-assembled film of vacuum-Sublimable functional molecule. Adv. Mater. **30**, 1705416 (2018)
11. Xue, S., Guo, Y., Rotaru, A., Müller-Bunz, H., Morgan, G.G., Trzop, E., Collet, E., Oláh, J., Garcia, Y.: Spin crossover behavior in a homologous series of Iron(II) complexes based on functionalized Bipyridyl ligands. Inorg. Chem. **57**, 9880 (2018)
12. Gillaizeau-Gauthier, I., Odobel, F., Alebbi, M., Argazzi, R., Costa, E., Bignozzi, C.A., Qu, P., Meyer, G.J.: Phosphonate-based Bipyridine dyes for stable photovoltaic devices. Inorg. Chem. **40**, 6073 (2001)
13. Schwab, P.F.H., Fleischer, F., Michl, J.: Preparation of 5-brominated and 5,5′-Dibrominated 2,2‘-Bipyridines and 2,2‘-Bipyrimidines. J. Org. Chem. **67**, 443 (2002)
14. Lagarec, K., Rancourt, D. G.: Recoil, Mössbauer Spectral Analysis Software for Windows 1.0. Department of Physics, University of Ottawa, Canada (1998)
15. Linares, J., Codjovi, E., Garcia, Y.: Pressure and temperature spin crossover sensors with optical detection. Sensors. **12**, 4479 (2012)
16. Boukheddaden, K., Ritti, M.H., Bouchez, G., Sy, M., Dîrtu, M.M., Parlier, M., Linares, J., Garcia, Y.: Quantitative contact pressure sensor based on spin crossover mechanism for civil security applications. J. Phys. Chem. C. **122**, 7597 (2018)