Subcomponent self-assembly of a Fe(III) based mononuclear complex with organosulfonate anion

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Abstract

Schiff-based ligands are good building blocks for iron complexes. In this work, a new mononuclear iron(III) complex based on hexadentate Schiff-based ligand with formula [Fe(3,2,3-sal$_2$tet)]***psca*** (3,2,3-sal$_2$tet = *N*, *N*', *N*'', *N*'''-1,5,8,12-tetraazadodecane-bis(salicylaldiminato), ***psca*** = *p*-sulfocinnamic acid) was papered by subcomponent self-assembly method. A photo-responsive anion, ***psca***, was incorporated into this system to study the effect of light-induced photo-isomerization of the anion on the spin state. ^{57}Fe Mössbauer spectroscopy was employed to study the spin state of the precursor Fe(II) salt ([Fe(H$_2$O)$_6$)](***psca***)$_2$·2H$_2$O) and the resulting iron(III) complex.

Keywords: *Fe(III) complexes ● psca ● ^{57}Fe Mössbauer spectroscopy ● spin state ● spin crossover*

1. Introduction

In recent years, coordination compounds have received increasing attention due to their ability to combine the functions of metal cations and organic molecules/anions as ligands into a single compound. Among them, spin crossover (SCO) compounds that can achieve transitions between low-spin (LS) and high-spin (HS) states at the molecular level are very attractive in thermal sensors, light switches, and information storage devices.[1-3] Countless Fe(II) spin-state complexes have been reported, however, iron(III) compounds have the advantage of being generally stable in air compared to iron(II) systems, and thus hold promise to be more amenable to processing in some devices.[4-7] Schiff base ligands are easily prepared by a simple one-pot condensation of aldehydes and primary amines in alcoholic solvents and are therefore widely used as ligands.[8-10] For example, Wilson *et. al* reported pseudo-octahedral Fe(III) complexes derived from triethylenetetramine (trien) and salicylaldehyde are in the LS state.[11] Hayami *et. al* studied the ligand field strength in a series of Fe(III) complexes, including [Fe(3,3,3-sal$_2$tet)]X, [Fe(3,2,3-sal$_2$tet)]X, [Fe(2,3,2-sal$_2$tet)]X, [Fe(2,2,2-sal$_2$tet)]X (X = NO_3^-, ClO_4^-, PF_6^-, and Cl^-), indicating that the spin state was directly affected by the length of the methylene chain in the ligand.[12] Recently, Kalita *et al*. reported a structurally characterized Fe(III) complex exhibiting thermally induced SCO behavior, demonstrating the critical role of subtle structural parameters and hydrogen bonding networks in tuning the spin state of iron(III) centers.[7]

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Anions play an important role in metal complexes, in particular counter anions, that after inclusion into a given crystal lattice, can significantly affect the spin state.[13-15] Among them, the anions with oxygen-rich functional groups have excellent contributions to hydrogen bonding and cooperativity.[16,17] Herein, we introduced ***psca***, an interesting organosulfonate anion, to study the possible anion effect on the spin state. In addition, as a derivative of *trans*-cinnamic acid, this anion is hopeful to undergo [2+2] photodimerization under UV light irradiation in the solid-state at room temperature.[18]

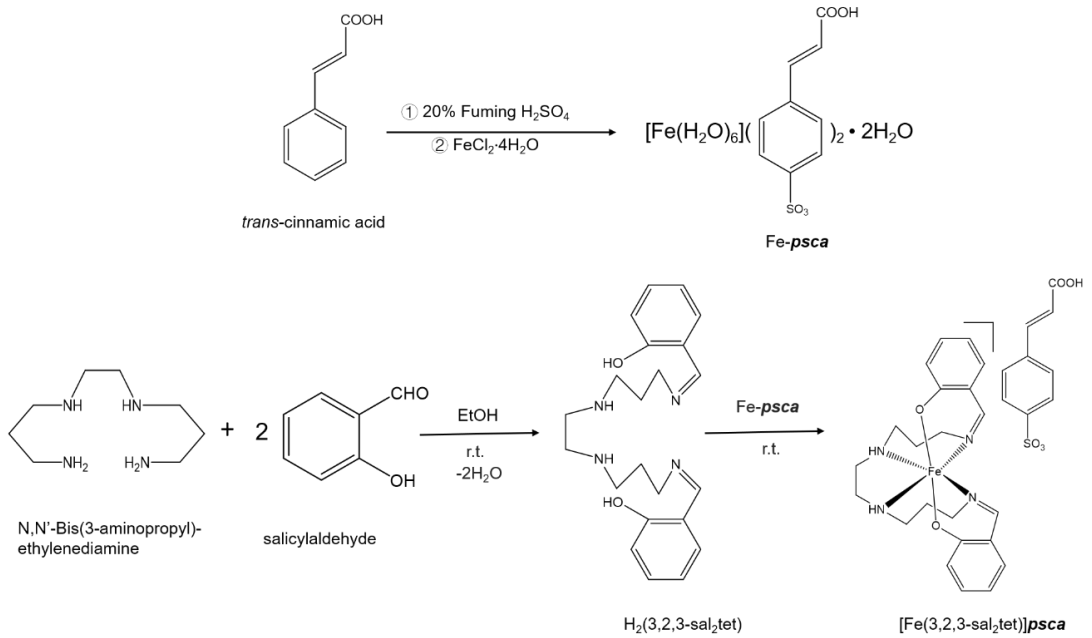

Fig. 1. Schematic representation of the formation for $[Fe(H_2O)_6)](\textbf{\textit{psca}})_2 \cdot 2H_2O$ and [Fe(3,2,3-sal_2tet)]***psca***.

2. Experimental

$[Fe(H_2O)_6](psca)_2$ was prepared by reported method.[19] [Fe(3,2,3-sal_2tet)]***psca*** was prepared as follows (**Fig. 1**): *N,N'*-Bis(3-aminopropyl)-ethylenediamine (0.175 g, 1 mmol) and salicylaldehyde (0.244 g, 2 mmol) was added into ethanol (20 mL) yielding a yellow colored solution. $[Fe(H_2O)_6)](\textbf{\textit{psca}})_2 \cdot 2H_2O$ (0.616 g, 1 mmol) was dissolved in ethanol (10 mL) in a separate beaker to get a clear solution. The above two solutions were mixed and stirred at room temperature for 30 min. The resulting solution was then filtrated and added to a test tube. Diethyl ether vapor was then allowed to diffuse into the test tube. Purple needle-like crystals were obtained in 4 days. The crystals were then removed from the small tube, washed with a small amount of ethanol and dried in the air. Yield: 31% (208 mg). [Fe(3,2,3-sal_2tet)]OTf and $[Fe(3,2,3\text{-}sal_2tet)]BF_4$ were obtained using $Fe(OTf)_2$ and $Fe(BF_4)_2$ as iron sources, respectively, following the same procedure described above, with crystals formed by slow evaporation under ambient conditions.

All chemicals and solvents were purchased from commercial sources of analytical grade and used without further purification. Fourier transform infrared spectroscopy recorded on a Shimadzu FTIR-8400S instrument using KBr particles was used to demonstrate the successful

synthesis of $[Fe(H_2O)_6)](\boldsymbol{psca})_2 \cdot 2H_2O$. High-resolution mass spectra in the positive-ion and negative-ion electrospray ionization (ESI) mode were obtained using a time TOF fleX Mass Spectrometer (Bruker Daltonics) operated with timsControl 3.1 software (Bruker Daltonics). ^{57}Fe Mössbauer spectroscopy data were collected by use of a constant-acceleration mode conventional spectrometer equipped with a 50 mCi ^{57}Co (Rh) source and a Reuter Stokes proportional counter. The microcrystalline sample was enclosed in a cylindrical plastic sample holder and spectra were recorded at room temperature. The spectra were fitted using Recoil 1.05 Mössbauer Analysis software[20] and the isomer shift values (δ) are given with respective to metallic iron at room temperature.

3. Results and discussion

The spectra of characteristic peaks of sulfonic acid and carboxyl groups in $[Fe(H_2O)_6)](\boldsymbol{psca})_2 \cdot 2H_2O$ are clearly shown in **Fig.2**: 1681 cm^{-1} (C=O), 1635 cm^{-1} (C=C), 1311 cm^{-1} (asym S=O), 1121 cm^{-1} (sym S=O), 829 cm^{-1} (S-O), which prove the successful synthesis of sulfonic acid iron salt. The high-resolution mass spectrum (ESI^+) exhibits a peak at *m/z* 436.1558, which is in excellent agreement with the calculated value of 436.1556 for the molecular ion $[Fe(3,2,3\text{-}sal_2tet)]^+$, further supporting the successful synthesis of the target iron complex.

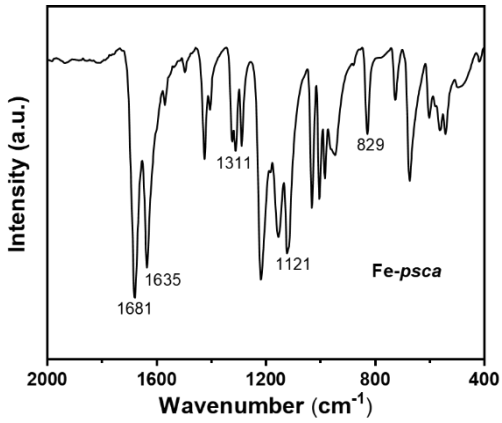

Fig. 2. Infrared spectrum of $[Fe(H_2O)_6)](\boldsymbol{psca})_2 \cdot 2H_2O$ over a selected range.

The spin states of $[Fe(H_2O)_6)](\boldsymbol{psca})_2 \cdot 2H_2O$ and $[Fe(3,2,3\text{-}sal_2tet)]\boldsymbol{psca}$ were studied by ^{57}Fe Mössbauer spectroscopy at room temperature in transmission mode. Related parameters are shown in **Table 1**. As shown in **Fig.3a**, the spectrum of $[Fe(H_2O)_6)](\boldsymbol{psca})_2 \cdot 2H_2O$ shows a major quadrupole doublet with an isomer shift δ = 1.26(5) mm s^{-1} and a quadrupole splitting ΔE_Q = 3.24(1) mm s^{-1} of area fraction A = 90.8%, which are characteristic of HS Fe(II) ions.[18] Another small quadrupole doublet characteristics of HS Fe(III) ions is detected (δ = 0.15 mm s^{-1}; ΔE_Q = 0.44(1) mm s^{-1}; A = 9.2%). This indicates that $[Fe(H_2O)_6)](\boldsymbol{psca})_2 \cdot 2H_2O$ was partially oxidized in air. The spectrum of $[Fe(3,2,3\text{-}sal_2tet)]\boldsymbol{psca}$ shows a quadrupole doublet with an isomer shift δ = 0.15(1) mm $s^{-1}$and a quadrupole splitting ΔE_Q = 2.18(2) mm s^{-1} diagnostic of Fe(III) ions in the LS state (**Fig 3b**). The parameters for each spin state are consistent with the data for previously reported Fe(III) complexes with N_4O_2 coordination sites[21]. Notably, a special feature of the Fe(III) system is that the spectrum is generally asymmetric compared to Fe(II),[22,23] which has been reported to be attributed to bond anisotropy and fast spin interconversion.[6,24,25]

Mössbauer data of [Fe(3,2,3-sal$_2$tet)]OTf and [Fe(3,2,3-sal$_2$tet)]BF$_4$ were also collected at room temperature. All compounds exhibit single doublets with parameters characteristic of LS Fe(III), confirming that the LS state is maintained across different counteranions. Notably, [Fe(3,2,3-sal-tet)]BF$_4$ shows a larger quadrupole splitting (ΔE_Q = 2.93(2) mm·s^{-1}) and broader line width ($\Gamma/2$ = 0.35(2) mm·s^{-1}), likely suggesting a slightly more distorted coordination environment.[26] These results support the conclusion that the spin state is predominantly determined by the rigid and symmetric coordination geometry of the Schiff base ligand around the iron ions, rather than by the nature of the counteranion.

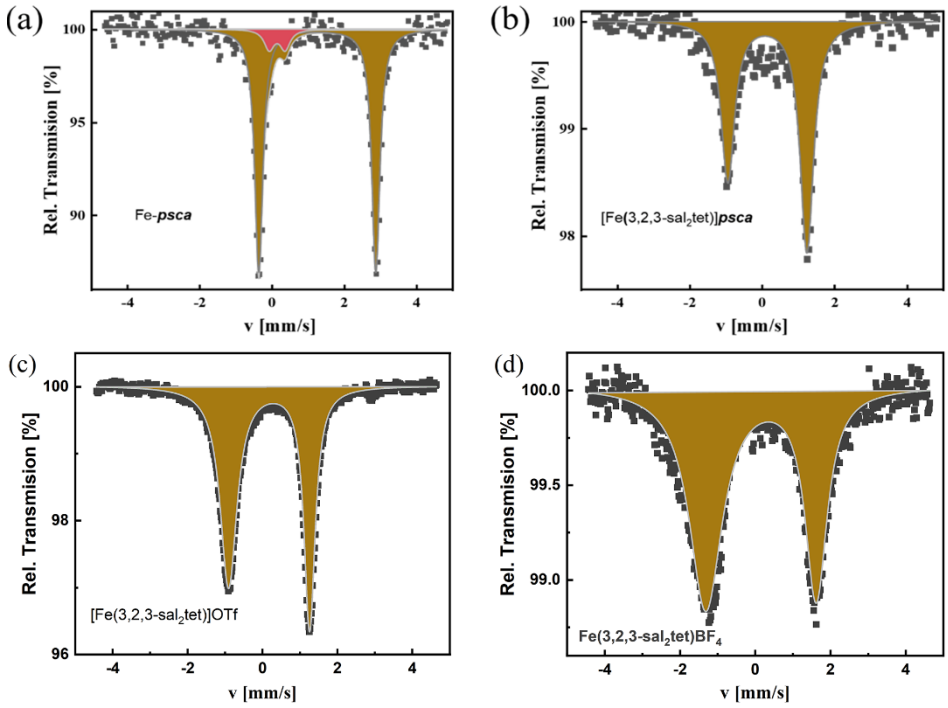

Fig. 3. ^{57}Fe Mössbauer spectra of (a) [Fe(H$_2$O)$_6$)](***psca***)$_2$·2H$_2$O, (b) [Fe(3,2,3-sal$_2$tet)]***psca***, (c) [Fe(3,2,3-sal$_2$tet)]OTf and (d) [Fe(3,2,3-sal$_2$tet)]BF$_4$ recorded at 298 K.

Table 1. Overview of selected ^{57}Fe Mössbauer parameters for complexes under study.

Complexes	**Spin state**	**Mössbauer parameters**			
		δ (mm s^{-1})	***ΔE$_Q$ (mm s^{-1})***	***Γ/2***	***fraction (%)***
[Fe(H$_2$O)$_6$)](***psca***)$_2$·2H$_2$O	Fe(II) HS	1.26(5)	3.24(1)	0.13(1)	90.8
	Fe(III) HS	0.15*	0.44(1)	0.17(1)	9.2
[Fe(3,2,3-sal$_2$tet)]***psca***	Fe(III) LS	0.15(1)	2.18(2)	0.22(1)	100
[Fe(3,2,3-sal$_2$tet)]OTf	Fe(III) LS	0.17(2)	2.16(3)	0.17(3)	100
[Fe(3,2,3-sal$_2$tet)]BF$_4$	Fe(III) LS	0.15(1)	2.93(2)	0.35(2)	100

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

4. Conclusions

In summary, we report a new mononuclear Fe(III) complex constructed by a Schiff base ligand and an organic sulfonic acid counterion (***psca***), which was prepared by a simple one-pot synthesis. From the ^{57}Fe Mössbauer spectrum, it is revealed that the Fe(II) ion in the sulfonic acid iron salt ($[Fe(H_2O)_6]$)(***psca***)$_2\cdot 2H_2O$) is in the high-spin state, while the Fe(III) ion in the [Fe(3,2,3-sal$_2$tet)]***psca*** complex is in the low-spin state. However, due to the strength of the ligand field was directly affected by the length of the methylene chain in the ligand, it is anticipated to obtain complexes with spin crossover by varying the number of methylene chains in the ligands. Furthermore, the anion derived from *trans*-cinnamic acid is expected to undergo [2+2] photodimerization at room temperature under Ultra-Violet light irradiation. This open good prospects for future research on this family of iron complexes.

Acknowledgements

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References

1. Gutlich, P.; Gaspar, A. B.; Garcia, Y., Spin state switching in iron coordination compounds. Beilstein J. Org. Chem. **9**, 342-91, (2013).
2. Garcia, Y.; Robert, F.; Naik, A. D.; Zhou, G.; Tinant, B.; Robeyns, K.; Michotte, S.; Piraux, L., Spin transition charted in a fluorophore-tagged thermochromic dinuclear iron(II) complex. J. Am. Chem. Soc. **133**, 15850-3, (2011).
3. Kahn, O.; Martinez, C. J., Spin-transition polymers: from molecular materials toward memory devices. Science. **279**, 44-48, (1998).
4. Garcia, Y.; Kahn, O.; Rabardel, L.; Chansou, B.; Salmon, L.; Tuchagues, J. P., Two-Step Spin Conversion for the Three-Dimensional Compound Tris (4, 4 '-bis-1, 2, 4-triazole) iron (II) Diperchlorate. Inorg Chem. **38**, 4663-4670, (1999).
5. Ohta, H.; Sunatsuki, Y.; Kojima, M.; Iijima, S.; Akashi, H.; Matsumoto, N., A tripodal ligand containing three imidazole groups inducing spin crossover in both Fe(II) and Fe(III) complexes; structures and spin crossover behaviors of the complexes. Chem Lett. **33**, 350-351, (2004).
6. Harding, D. J.; Harding, P.; Phonsri, W., Spin crossover in iron(III) complexes. Coordin Chem Rev. **313**, 38-61, (2016).
7. Kalita, A. J. H. A., Reductive nitrosylation of Iron (III) complexes of tetradentate ligands. **4**, 100104, (2023).
8. Sundaresan, S.; Kühne, I.; Kelly, C.; Barker, A.; Salley, D.; Müller-Bunz, H.; Powell, A.; Morgan, G., Anion influence on spin state in two novel Fe(III) compounds: [Fe(5F-sal2333)]X. Crystals. **9**, (2018).
9. Brewer, C. T.; Brewer, G.; Jameson, G. B.; Kamaras, P.; May, L.; Rapta, M., Structure and magnetism of electronically distorted iron(III) Schiff-base complexes. J Chem Soc, Dalton Trans. 37-43, (1995).
10. Oyedepo, B. M.; Aremu, J. A.; Ejeromedoghene, O.; Omoniyi, A. O.; Adewuyi, S., Development of Chitosan Schiff base-Stabilized metal nanoparticles for the catalytic hydrodechlorination of 2-chlorophenol. Hybrid Advances. **9**, (2025).

11. Tweedle, M. F.; Wilson, L. J., Variable spin iron (III) chelates with hexadentate ligands derived from triethylenetetramine and various salicylaldehydes. Synthesis, characterization, and solution state studies of a new ^{2}T. dblarw. ^{6}A spin equilibrium system. J.Am. Chem. Soc. **98**, 4824-4834, (1976).
12. Hayami, S.; Matoba, T.; Nomiyama, S.; Kojima, T.; Osaki, S.; Maeda, Y., Structures and magnetic properties of some Fe(III) complexes with hexadentate ligands: in connection with spin-crossover behavior. B Chem Soc Jpn. **70**, 3001-3009, (1997).
13. Klug, C. M.; McDaniel, A. M.; Fiedler, S. R.; Schulte, K. A.; Newell, B. S.; Shores, M. P., Anion dependence in the spin-crossover properties of a Fe(II) podand complex. Dalton Trans. **41**, 12577-85, (2012).
14. Nemec, I.; Herchel, R.; Šalitroš, I.; Trávníček, Z.; Moncoľ, J.; Fuess, H.; Ruben, M.; Linert, W., Anion driven modulation of magnetic intermolecular interactions and spin crossover properties in an isomorphous series of mononuclear iron(III) complexes with a hexadentate Schiff base ligand. CrystEngComm. **14**, (2012).
15. Dîrtu, M. M.; Rotaru, A.; Gillard, D.; Linares, J.; Codjovi, E.; Tinant, B.; Garcia, Y., Prediction of the spin transition temperature in Fe(II) one-dimensional coordination polymers: an anion based database. Inorg Chem. **48**, 7838-52, (2009).
16. Garcia, Y.; Van Koningsbruggen, P. J.; Codjovi, E.; Lapouyade, R.; Kahn, O.; Rabardel, L., Non-classical Fe II spin-crossover behaviour leading to an unprecedented extremely large apparent thermal hysteresis of 270 K: application for displays. J. Mater. Chem. **7**, 857-858, (1997).
17. Zhao, X. H.; Zhang, S. L.; Shao, D.; Wang, X. Y., Spin Crossover in [Fe(2-Picolylamine)$_3$]$^{2+}$ Adjusted by Organosulfonate Anions. Inorg Chem. **54**, 7857-67, (2015).
18. Kumar, V.; Fusaro, L.; Aprile, C.; Robeyns, K.; Garcia, Y., [2 + 2] Photodimerization of sulfonate derivative of trans-cinnamic acid: kinetics study using solid state ^{13}C NMR and hybrid material inclusion. Cryst Growth Des. **20**, 7850-7861, (2020).
19. Kumar, V.; El-Massaoudi, M.; Radi, S.; Van Hecke, K.; Rotaru, A.; Garcia, Y., Iron(ii) coordination pyrazole complexes with aromatic sulfonate ligands: the role of ether. New J Chem. **44**, 13902-13912, (2020).
20. Lagarec, K.; Rancourt, D. G., Recoil-Mössbauer spectral analysis software for Windows. University of Ottawa, Ottawa, 1998.
21. Hayami, S.; Matoba, T.; Nomiyama, S.; Kojima, T.; Osaki, S.; Maeda, Y., Structures and magnetic properties of some Fe(III) complexes with hexadentate ligands: in connection with spin-crossover behavior. B Chem Soc Jpn. **70**, 3001-3009, (1997).
22. Murnaghan, K. D.; Carbonera, C.; Toupet, L.; Griffin, M.; Dîrtu, M. M.; Desplanches, C.; Garcia, Y.; Collet, E.; Letard, J. F.; Morgan, G. G., Spin-state ordering on one sub-lattice of a mononuclear iron(III) spin crossover complex exhibiting LIESST and TIESST. Chem. **20**, 5613-8, (2014).
23. Griffin, M.; Shakespeare, S.; Shepherd, H. J.; Harding, C. J.; Letard, J. F.; Desplanches, C.; Goeta, A. E.; Howard, J. A.; Powell, A. K.; Mereacre, V.; Garcia, Y.; Naik, A. D.; Muller-Bunz, H.; Morgan, G. G., A symmetry-breaking spin-state transition in iron(III). Angew Chem Int Ed Engl. **50**, 896-900, (2011).
24. Harding, D. J.; Sertphon, D.; Harding, P.; Murray, K. S.; Moubaraki, B.; Cashion, J. D.; Adams, H., Fe(III) quinolylsalicylaldimine complexes: a rare mixed-spin-state complex and abrupt spin crossover. Chem. **19**, 1082-90, (2013).
25. Vieira, B. J.; Coutinho, J. T.; Santos, I. C.; Pereira, L. C.; Waerenborgh, J. C.; da Gama, V., [Fe(nsal$_2$trien)]SCN, a new two-step iron(III) spin crossover compound, with symmetry breaking spin-state transition and an intermediate ordered state. Inorg Chem. **52**, 3845-50, (2013).
26. Garcia, Y.; Wang, J.; Zhang, T. 'Mössbauer Spectroscopy: Applications in Chemistry and Materials Science' Wiley VCH (2024).