

A dinuclear iron(II) complex, [(TPyA)Fe^{II}(THBQ²⁻)Fe^{II}(TPyA)](BF₄)₂ [TPyA = tris(2-pyridylmethyl)amine; THBQ²⁻ = 2,3,5,6-tetrahydroxy-1,4-benzoquinonate] exhibiting both spin crossover with hysteresis and ferromagnetic exchange

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Dinuclear [(TPyA)Fe^{II}(THBQ²⁻)Fe^{II}(TPyA)](BF₄)₂ (**1**) possesses hydrogen bonding interactions that form a 1-D chain, and π - π interactions between the 1-D chains that give rise to a 2-D supramolecular-layered structure, inducing hysteresis in the spin crossover behavior; **1** has shown spin crossover behavior around 250 K with thermal hysteresis and ferromagnetic interactions at low temperature.

Multifunctional magnetic materials have attracted attention because of their potential use as electronic switches, displays, and data storage devices.¹ In particular, spin crossover (SCO) materials are very useful for these aims in which physical properties can be tuned by external stimuli, *i.e.* temperature, light, and/or pressure.² Many metal complexes with chloranilate (CA²⁻) analogues have been studied because of their interesting redox and magnetochemistry, due to the noninnocent nature of this delocalized π system.³ Recently, dinuclear Fe(II) complexes exhibiting spin crossover behavior or ferromagnetic coupling have been reported for [(TPyA)Fe^{II}(DBQ²⁻)Fe^{II}(TPyA)](BF₄)₂, DBQ²⁻ = 2,5-di-*tert*-butyl-3,6-dihydroxy-1,4-benzoquinonate; TPyA = tris(2-pyridylmethyl)amine; and [(TPyA)Fe^{II}(CA²⁻)Fe^{II}(TPyA)](BF₄)₂, respectively.⁴ Although the former displays SCO behavior around room temperature, it does not exhibit thermal hysteresis. Thus, to induce thermal hysteresis, greater interdimer cation interactions were sought, and introduction of interdimer H-bonding was targeted. Hence, 2,3,5,6-tetrahydroxy-1,4-benzoquinone (H₂THBQ) was identified as a bridging ligand, and we report [(TPyA)Fe^{II}(THBQ²⁻)Fe^{II}(TPyA)](BF₄)₂ (**1**)† and its coexisting spin crossover with thermal hysteresis behaviors in addition to an intradimer ferromagnetic interaction.

The structure of **1** was determined at 208 (Fig. 1) and 295 K.‡ Each Fe(II) ion in the dinuclear [(TPyA)Fe^{II}(THBQ²⁻)Fe^{II}(TPyA)]²⁺ cation has a distorted octahedral geometry with the four nitrogen atoms of TPyA and the two oxygen atoms of

THBQ²⁻ in the *cis* positions. The asymmetric unit consists of two halves of two independent Fe(II) dimers, each possessing a crystallographic center of symmetry at both 208 and 295 K. The two unique dinuclear compounds in an asymmetric unit at 208 K have similar structures, but have very different bond lengths around the Fe^{II}.

At 208 K the average Fe–O and Fe–N bond distances are 1.953(2) and 1.958(2) Å in one asymmetric unit, and 2.089(2) and 2.180(2) Å in the other asymmetric unit. Thus, the former unique dinuclear complex is predominantly low spin (LS), while the other is predominantly high spin (HS). The latter HS species has longer Fe–O and Fe–N distances with respect to the LS species by 0.136 and 0.222 Å, respectively, due to the Fe(II) spin states difference at 208 K.⁵ Hence, the unit cell is composed of two dinuclear Fe(II) complexes, one with spin singlet and the other with quintet Fe(II) sites. The cell volume increases by 149 Å³ (3.2%) upon warming from 208 to 295 K. The average Fe–O and Fe–N bond distances at 295 K are 2.087(3) and 2.163(2) Å for the asymmetric unit. The

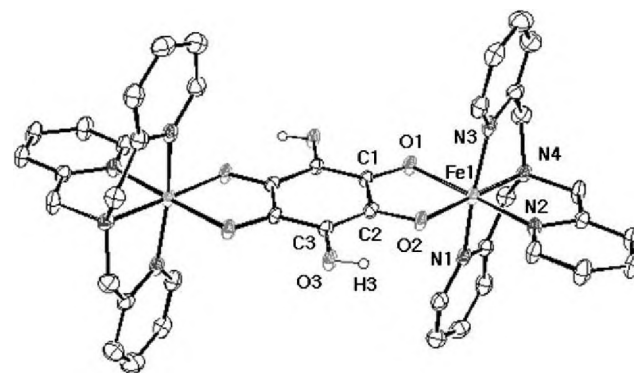


Fig. 1 ORTEP (30% probable thermal ellipsoid) view of **1** at 208 K. The dication with predominately HS Fe(II)s in **1** is similar and not shown. H atoms of carbon and BF₄⁻ are omitted for clarity. Key distances (Å) and angles (°): asymmetric unit with predominately LS Fe(II)s: Fe1–O1 1.974(3), Fe1–O2 1.931(3), Fe1–N1 1.984(4), Fe1–N2 1.930(3), Fe1–N3 1.955(4), Fe1–N4 1.973(3), C1–C2 1.486(5), C2–C3 1.387(5), C3–C1' 1.391(5), C1–O1 1.285(4), C2–O2 1.290(4), C3–O3 1.368(4), O1–Fe1–O2 83.22(11). Asymmetric unit with predominately HS Fe(II)s: Fe1–O1 2.148(3), Fe1–O2 2.029(3), Fe1–N1 2.175(4), Fe1–N2 2.145(3), Fe1–N3 2.168(4), Fe1–N4 2.223(3), C1–C2 1.523(5), C2–C3 1.362(5), C3–C1' 1.402(5), C1–O1 1.254(4), C2–O2 1.284(4), C3–O3 1.377(4), O1–Fe1–O2 77.71(10).

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difference in the average Fe–L bond distances disappears upon warming to 295 K, indicating that both dinuclear complexes are predominantly high spin states at room temperature. The average C–O and C1–C2 bond distances of THBQ²⁻ are 1.288(3) and 1.486(5) Å for the dimer possessing LS Fe(II)s, and 1.269(3) and 1.523(5) Å for the dimer possessing HS Fe(II)s. In the HS species of **1**, the C–O and C–C bond lengths are clearly in good agreement with those of a CA²⁻ type ligand.⁴ However, in LS species the bond lengths of C–O and C–C lie in middle of CA²⁻ and CA³⁻ type ligands. This is attributed to the low-spin Fe(II) ion. That is, a low-spin Fe(II) ion bonds to the O atom of the THBQ²⁻ ligand more strongly than a high-spin Fe(II) ion as shown in the structure. The average C2–C3 and C3–C1' bond lengths are 1.389(4) Å for the dimers possessing LS Fe(II)s and 1.382(4) Å for the dimer possessing HS Fe(II)s, showing that the bonds are delocalized regardless of the Fe(II) spin states.

Based upon the bond distances, the THBQ²⁻ ions in the two different dinuclear complexes in **1** are slightly different from each other, due to the LS and HS states of the Fe(II) ions. This confirms *S* = 0 THBQ²⁻ bridged ligands, not spin-bearing THBQ³⁻, in accord to that reported for [(TPyA)Co(CA)Co(TPyA)]⁺.^{4b} The shortest intradimer Fe···Fe separation is 7.614(1) Å and is 18% greater than the shortest interdimer Fe···Fe distance of 6.448(1) Å.

As anticipated, intermolecular O–H···O hydrogen bonding interactions exist between the hydroxyl groups of THBQ²⁻ ions, giving rise to a 1-D chain motif.⁶ Interestingly, the 1-D chains consist of ···ABAB··· units. The TPyA pyridyl groups are involved in offset face-to-face π – π interactions between the Fe(II) dimers in a 1-D polymer and between the 1-D chains,⁷ in which complex **1** gives rise to 2-D supramolecular layered structure.

The 2–350 K magnetic susceptibility, χ , was obtained on a SQUID magnetometer (Fig. 2). At 350 K, the effective moment, μ_{eff} [= ((3*k*_B/*N* μ_{B} ³) χT)^{1/2}], is 7.34 μ_{B} /Fe₂, and decreases slightly with decreasing temperature to 7.24 μ_{B} /Fe₂ at 270 K, followed by an abrupt decrease to 5.77 μ_{B} /Fe₂ at 230 K, indicating a spin crossover behavior related to the high and low spin transition of the Fe dimer (**1**). Fig. 2 (inset) shows the thermal dependence of the μ_{eff} (*T*) upon warming and cooling. Upon cooling, the μ_{eff} (*T*) value abruptly drops from 6.86 μ_{B} /Fe₂ at 255 K to 5.76 μ_{B} /Fe₂ at 215 K. As shown in Fig. 2 (inset), the magnetic moment recovered to the original values after both warming and cooling. The width

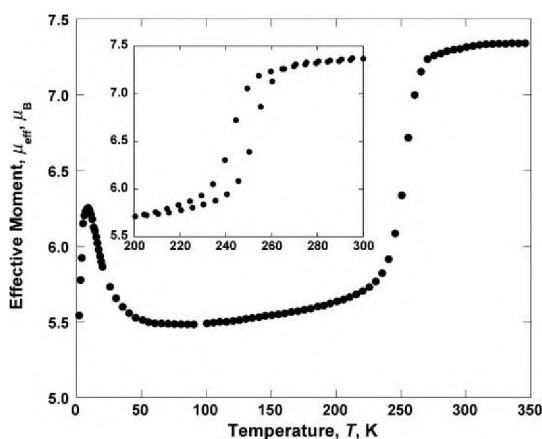


Fig. 2 μ_{eff} (*T*) per asymmetric unit for **1** at 1 kOe upon warming and thermal hysteresis around 250 K (inset).

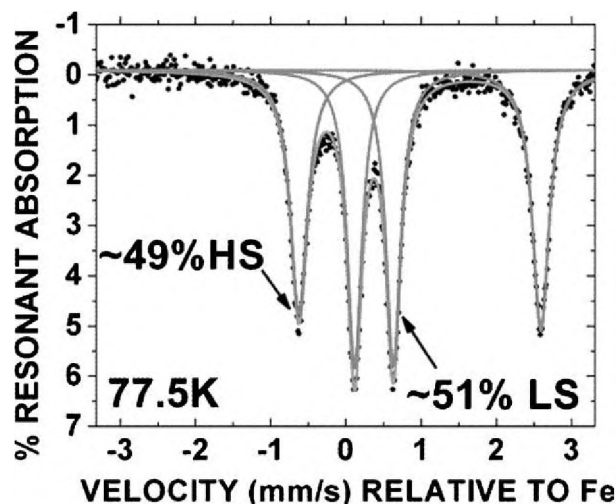


Fig. 3 Mössbauer spectrum of **1** confirming intensity LS \approx intensity HS, fully consistent with X-ray results [$\delta_{\text{LS}} = 0.37 \text{ mm s}^{-1}$, $\Delta E_{\text{LS}} = 0.52 \text{ mm s}^{-1}$; $\delta_{\text{HS}} = 0.98 \text{ mm s}^{-1}$, $\Delta E_{\text{HS}} = 3.21 \text{ mm s}^{-1}$].

of the thermal hysteresis was *ca.* 10 K. Remarkably, after the SCO μ_{eff} (*T*) gradually decreases with decreasing temperature to 5.53 μ_{B} /Fe₂ at 45 K, then it increases to maximum of 6.25 μ_{B} /Fe₂ at 9 K, indicative of a ferromagnetic interaction between the Fe(II) centers, and again decreases to 5.54 μ_{B} /Fe₂ at 2 K due to the interdimer antiferromagnetic exchange and/or zero field splitting. Unexpected ferromagnetic coupling as observed for **1** has been reported for [(TPyA)Fe(CA)Fe(TPyA)](BF₄)₂ (*J*/*k*_B = +1.0 K).^{4b} Surprisingly, **1** exhibits dual magnetic properties, such as a spin transition at \sim 250 K with thermal hysteresis (width \approx 10 K) as well as a ferromagnetic coupling below 45 K. The existence of the hysteresis effect can be attributed to hydrogen bonding interactions between hydroxyl groups of bridged THBQ²⁻ ligand in **1**.⁸ The rise in μ_{eff} (*T*) at low temperature suggests the onset of magnetic coupling and is under further investigation.

The Mössbauer spectrum of **1** gives evidence of incipient formation of LS Fe(II) at room temperature while SCO behavior is obvious at \sim 270 K in accord with the SQUID data. The combination of Mössbauer spectroscopy and X-ray results for **1** definitively confirm the presence of dinuclear pairs of Fe(II) for which one pair is all HS and the other is all LS, as opposed to 50 : 50 LS : HS within *each* dinuclear Fe(II) complex at 77 K (Fig. 3). The zero field Mössbauer spectrum of Fig. 3 does not distinguish the latter possibility by itself.⁹

In conclusion, the first dinuclear Fe(II) complex bridged with a tetraoxolene-type ligand, exhibiting the dual magnetic functions of a spin crossover with hysteresis and a ferromagnetic interaction, is reported. Further studies on the mechanism of the SCO and fabrication of new dinuclear complexes showing a hysteresis at room temperature are ongoing.

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Notes and references

† **Synthesis:** **1** was synthesized from a MeOH solution (50 mL) of [Fe(OH₂)₆](BF₄)₂ (232 mg, 0.688 mmol) added to MeOH solutions (10 mL)

of TPyA (200 mg, 0.688 mmol) and H₂THBQ (39 mg, 0.344 mmol) in a wet box (<1 ppm O₂). The solution turned dark brown, was neutralized with NEt₃ (0.20 mL, 1.38 mmol), and heated to reflux for 1 h. After filtration while hot, the filtrate was allowed to stand at room temperature for 2 or 3 days. Dark brown crystals formed which were collected by filtration, washed with MeOH, and dried *in vacuo* to afford 195 mg (55%) of **1**. IR (KBr): ν_{OH} 3406, ν_{CH} 3069, 2924, ν_{CN} 1604, ν_{CO} 1531, ν_{BF} 1053 cm⁻¹. Anal. calcd for C₄₂H₃₈B₂F₈Fe₂N₈O₆: C, 48.69; H, 3.70; N, 10.81. Found: C, 48.83; H, 3.75; N, 10.36%.

‡ **Crystal and structure refinement parameters for 1**: At 208(2) K, C₄₂H₃₈B₂F₈Fe₂N₈O₆, fw = 1036.12 g mol⁻¹, monoclinic, space group *P2₁/c*, *a* = 14.414(2) Å, *b* = 21.922(2) Å, *c* = 14.955(2) Å, β = 97.225(2)°, *V* = 4688.0(9) Å³, *Z* = 4, d_{calcd} = 1.468 g cm⁻³, $\mu(\text{MoK}\alpha)$ = 0.705 mm⁻¹, R_{int} = 0.0979, *R*1 = 0.0653, *wR*2 = 0.1260 (*I* > 2 σ (*I*)). CCDC 662710. At 295(2) K, monoclinic, space group *P2₁/c*, *a* = 15.190(1) Å, *b* = 21.590(1) Å, *c* = 14.818(1) Å, β = 95.508(1)°, *V* = 4837.2(3) Å³, *Z* = 4, d_{calcd} = 1.423 g cm⁻³, $\mu(\text{MoK}\alpha)$ = 0.683 mm⁻¹, R_{int} = 0.0906, *R*1 = 0.1053, *wR*2 = 0.3040 (*I* > 2 σ (*I*)). CCDC 662711. Data were collected on Bruker SMART/Enraf-Nonius KappaCCD automatic diffractometers using graphite monochromated MoK α (λ = 0.71073 Å) radiation. Structures were solved by direct methods and refined by full-matrix least-squares refinement using the SHELXL97¹⁰ programs. For crystallographic data in CIF or other electronic format, see DOI: 10.1039/b715271j

- 1 (a) O. Kahn and C. J. Martinez, *Science*, 1998, **279**, 44; (b) A. B. Gaspar, V. Ksenofontov, M. Seredyuk and P. Gülich, *Coord. Chem. Rev.*, 2005, **249**, 2661; (c) M. Nihei, M. Ui, M. Yokota, L. Han, A. Maeda, H. Kishida, H. Okamoto and H. Oshio, *Angew. Chem., Int. Ed.*, 2005, **44**, 6484; (d) O. Sato, J. Tao and Y.-Z. Zhang, *Angew. Chem., Int. Ed.*, 2007, **46**, 2152.
- 2 (a) *Spin Crossover in Transition Metal Compounds I*, ed. P. Gülich and H. A. Goodwin, Springer, New York, 2004, vol. 233; (b) J. A. Real, A. B. Gaspar, V. Niel and M. Muñoz, *Coord. Chem. Rev.*, 2003, **236**,

121; (c) S. Bonhommeau, T. Guillon, L. M. L. Daku, P. Demont, J. S. Costa, J.-F. Létard, G. Molnar and A. Bousseksou, *Angew. Chem., Int. Ed.*, 2006, **45**, 1625.

- 3 (a) S. Kitagawa and S. Kawata, *Coord. Chem. Rev.*, 2002, **224**, 11; (b) J. Tao, H. Maruyama and O. Sato, *J. Am. Chem. Soc.*, 2006, **128**, 1790.
- 4 (a) K. S. Min, A. DiPasquale, A. L. Rheingold and J. S. Miller, *Inorg. Chem.*, 2007, **46**, 1048; (b) K. S. Min, A. G. DiPasquale, J. A. Goien, A. L. Rheingold and J. S. Miller, *J. Am. Chem. Soc.*, 2007, **129**, 2360.
- 5 (a) D. L. Reger, J. R. Gardinier, W. R. Gemmill, M. D. Smith, A. M. Shabin, G. J. Long, L. Rebbouh and F. Grandjean, *J. Am. Chem. Soc.*, 2005, **127**, 2303; (b) S. Alvarez, *J. Am. Chem. Soc.*, 2003, **125**, 6795; (c) N. Bréfuel, S. Inatomi, H. Torigoe, H. Hagiwara, S. Shova, J.-F. Meunier, S. Bonhommeau, J.-P. Tuchagues and N. Matsumoto, *Inorg. Chem.*, 2006, **45**, 8126; (d) K. W. Törnroos, M. Hostettler, D. Chernyshov, B. Vangdal and H.-B. Bürgi, *Chem.-Eur. J.*, 2006, **12**, 6207.
- 6 At 208 K, O3 \cdots O3B = 2.802(4) Å, \angle O3–H3–O3B = 148.32°; O3B \cdots F4(–*x* + 1, –*y*, –*z* + 1) = 2.641(4) Å, \angle O3B–H3B–F4 = 153.35°. At 295 K, O3 \cdots O3B(*x*, –*y* + 1/2, *z* – 1/2) = 2.764(7) Å, \angle O3–H3–O3B = 150.15°; O3B \cdots F4(–*x*, *y* + 1/2, –*z* + 1/2) = 2.623(9) Å, \angle O3B–H3B–F4 = 151.89°.
- 7 (a) G. R. Desiraju, *Crystal Engineering: The Design of Organic Solids*, Elsevier, New York, 1989, ch. 4; (b) A. S. Shetty, J. Zhang and J. S. Moore, *J. Am. Chem. Soc.*, 1996, **118**, 1019.
- 8 H. Hagiwara, S. Hashimoto, N. Matsumoto and S. Lijima, *Inorg. Chem.*, 2007, **46**, 3136.
- 9 In the absence of X-ray data, these possibilities have been distinguished for SCO Fe(II) dimers *via* applied field Mössbauer spectroscopy. V. Ksenofontov, H. Spiering, S. Reiman, Y. Garcia, A. Gaspar, N. Moliner, J. Real and P. Gülich, *Chem. Phys. Lett.*, 2001, **348**, 381.
- 10 G. M. Sheldrick, *SHELXL-97, Program for refinement of crystal structures*, University of Göttingen, Germany, 1997.