Spin-State Patterning in an Iron(II) Tripodal Spin-Crossover Complex

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ABSTRACT: A mononuclear iron(II) complex that displays a gradual two-step spin-crossover (SCO) transition is reported. The intermediate plateau (IP) occurs between HS0.40LS0.60 and HS0.60LS0.40 (HS = high spin; LS = low spin) ratios over the region of ca. 190–170 K. A phase change occurs at the IP, breaking the symmetry, resulting in six independent SCO sites compared to one at the 100% HS and LS plateau regions, respectively. Variable-temperature X-ray photoelectron spectroscopy shows that the SCO behavior is completely reversible among the HS, IP, and LS regions. The results both confirm and extend the related results for the above system described by Halcrow et al. (Kulmaczewski, R.; Cespedes, O.; Halcrow, M. A. Gradual Thermal Spin-Crossover Mediated By a Reentrant and Extend the Related Results for the Above System Described by Halcrow et al. Inorg. Chem. 2017, 56, 3144–3148) in a recent report.

INTRODUCTION

Spin-crossover (SCO) materials show significant promise for application in several emerging technologies, including molecular switches, sensors, displays, molecular electronics, and spintronics.1–4 Although a large number of such materials have been developed, leading to a good understanding of the intramolecular properties (choice of metal ion, donor atom, sterics, etc.)5–11 that affect spin transitions in discrete complexes, the results of cooperative intramolecular effects (leading to hysteresis, sharp transitions, etc.)5,12 are still not readily predictable. This is particularly the case for supramolecular effects involving weak noncovalent interactions and/or crystal packing.13–18 Extremely recently, Halcrow et al.19 have reported the crystal structure and SCO properties of [FeL·(BF4)2]2 (L = tris(2-(((E)-thiazol-4-ylmethylene)amino)ethyl)amine), which features a two-step spin transition together with a symmetry-breaking phase change. Illustrating the immense interest in the field, we had been simultaneously and independently investigating the same material. Our results are largely consistent with those of Halcrow et al.19 Here, we present complementary results, including the high-resolution crystal structure of the intermediate phase (190 K), that clarify the symmetry-breaking nature of the phase transition: variable-temperature magnetic susceptibility measurements with slow scan rates, and variable-temperature X-ray photoelectron spectroscopy (VT-XPS).

RESULTS AND DISCUSSION

The [FeL·(BF4)2]2 (Figure 1) complex was prepared in a similar manner to that reported by Halcrow et al.,19 and we prepared single crystals by the slow diffusion of diethyl ether into an acetonitrile solution. The composition and purity of [FeL·(BF4)2]2 revealed the presence of a complete nonhysteretic SCO transition with a two-step character (Figure 2). These results are consistent with those of Halcrow et al.19 The two-step character arises from a change in slope over the region of ca. 190–170 K, representative of an intermediate plateau (IP) (however with declining rather than stable \( \chi_M T \) values). At 190 K, the \( \chi_M T \) value of ca. 1.25 cm\(^3\) mol\(^{-1}\) K corresponds to a high spin (HS)/low spin (LS) ratio of ca. 40.60 of Fe(II) sites, which drops to an HS/LS ratio of ca. 30.70 by 170 K.

VT-XPS (Figure 3 and see Supporting Information) showed the expected changes arising from the spin state on the Fe 2p\(_{1/2}\)
On X-ray ionization, compounds of the 3d transition metals undergo a coupling between the ionized 2p shell and the 3d shell to form multiplets, with an intensity dependent on the number of unpaired electrons in the 3d shell. Hence, the Fe 2p$_{3/2}$ peak of the HS complex at 298 K splits into relatively intense multiplets (peaks B−D). On cooling to 190 K, the combined normalized intensity of multiplets B−D decreases (inset in Figure 4), until a typical LS Fe(II) spectrum is observed at 100 K. The spin behavior is completely reversible, with the HS spectrum observed on warming to 298 K.

We also determined single-crystal X-ray structures of the HS state (298 K), the intermediate phase (190 K), and the LS state (100 K) (Table S1). Whereas the HS and LS structures are consistent with Halcrow’s results, the previous report on the structure of the symmetry-broken intermediate phase ($Z' = 6$, compared to $Z' = 1$ at room and low temperature) determined at 175 K “has relatively low precision, reflecting the size of the model and significant cation and anion disorder, which was only partly resolvable.” With careful attention to obtaining a suitable crystal, we were able to obtain data of high quality and without substantial disorder.

Detailed analysis (average Fe−N bond lengths and relative Fe(II) octahedral distortion) reveals two HS (Fe(2) and Fe(3)), two LS (Fe(4) and Fe(6)), and two mixed HS−LS Fe(II) sites (Fe(1) and Fe(5)) at 190 K (Figure 4). The spin-state assignment for the complete HS and LS sites was clear on the basis of the average Fe−N bond lengths and relative octahedral distortion at these sites (Table S1). On the basis of the complete HS and LS values above, respectively, the mixed HS−LS Fe(II) sites (i.e., of short-range crystallographic order) are of more LS character than HS. This assignment of short- and long-range ordered HS and LS states over the six distinct Fe(II) sites correlates well with the 40:60 HS/LS ratio observed.
magnetically at this temperature (Figure 2). We note that the detailed structural analysis reported on this phase by Halcrow et al. was conducted at 175 K, revealing three LS, one HS, and two mixed HS−LS Fe(II) sites, representative of a 30:70 HS/LS ratio as per magnetic measurements. From this, it is interesting then to observe that one of the mixed HS−LS sites attains a complete LS character over the duration of the “sloped” IP temperature range (i.e., 190−170 K).

The [FeL]^{2+} cations at 190 K are arranged in three distinct dimers comprising two mixed spin-state pairs (HS−LS) and one LS state pair (LS−LS) (Figure 4). These three unique pairs are distributed in distinct one-dimensional (1D) chains along...
the α-direction, as illustrated in Figure S. Spin-state/dimer confinement is also evident when viewed along the β-direction (Figure Sb). The origin for the molecular arrangement of Fe(II) spin states along the 1D chains is likely driven by lattice cooperativity, which arises from packing and short spin-center separations. This produces molecular-level spin-state domain formation within the 1D chains, which is conferred to a 3D spin-state patterning.

■ CONCLUSIONS

We have verified the findings of Halcrow et al.,19 which describes a new discrete mononuclear Fe(II) tripod complex that displays a two-step SCO behavior. At the intermediate phase, six independent spin sites are present, resulting in 3D spin-state patterning. Although there are no particular structural features and/or interactions that obviously contribute to this distinctive phase transition and rare spin-state patterning, we note that the overall strain involved in the hexadentate ligand type to accommodate the HS to LS transition may be a contributing factor.

■ METHODS

Materials. All chemicals and solvents used were of commercial grade and used without further purification.

Experimental Section. L Tris(2-aminooethyl)-amine (104 mg, 0.71 mmol) in 10 mL of ethanol was added to a solution of thiazole-4-carboxaldehyde (250 mg, 2.21 mmol) in 10 mL of ethanol, leading to the formation of a clear yellow solution. The residuum after the removal of the solvent was dissolved in acetonitrile for recrystallization. The crystallized product was washed with cold acetonitrile (3 × 5 mL) to give a light yellow solid in 67% yield.1H NMR (CDCl3, 300 MHz) (ppm): 8.79 (d, 3H), 8.39 (s, 3H), 7.72 (d, 3H), 3.73 (t, 6H, −CH2−), 2.96 (t, 6H, −CH2−); 13C NMR (dimethyl sulfoxide (DMSO), 75.5 MHz) (ppm): 254.99 (−C=O); UV−vis (solid state in nujol): 3024, 2926, 2844, 2809, 2781, 2741, 2637, 2549, 2520; FT−IR (50 mg, 0.12 mmol) in 10 mL of acetonitrile was slowly added to a suspension of L (50 mg, 0.12 mmol) in 10 mL of acetonitrile; there was an immediate color change from yellow to red. The mixture was heated at reflux for 3 h, and then the resulting yellow solution was left at 70 °C with overnight stirring. The residue obtained after the removal of the solvent was dissolved in acetonitrile for recrystallization. The crystallized product was washed with cold acetonitrile (3 × 5 mL) to give a light yellow solid in 67% yield.1H NMR (CDCl3, 300 MHz) (ppm): 8.79 (d, 3H), 8.39 (s, 3H), 7.72 (d, 3H), 3.73 (t, 6H, −CH2−), 2.96 (t, 6H, −CH2−); 13C NMR (dimethyl sulfoxide (DMSO), 75.5 MHz) (ppm): 155.63, 154.63, 153.15, 119.73, 60.08 (−CH2−), 55.43 (−CH2−); UV−vis (solid state in nujol): €νmax 256 nm; FT−IR (ATR κmax/cm−1): 3024, 2926, 2844, 2809, 1650, 1540, 1427, 1408, 1342, 1294, 1240, 1149, 1071, 1021, 938, 883, 858, 822, 755, 557, 491, 485, 413; ESI−HRMS (positive−ion detection, EtOH): m/z = 454.0942 [Na + L•FeL](BF4)2 (1) Iron(II) tetrafluoroborate hexahydrate (41 mg, 0.12 mmol) in 10 mL of acetonitrile was slowly added to a suspension of L (50 mg, 0.12 mmol) in 10 mL of acetonitrile; there was an immediate color change from yellow to red. The reaction mixture was heated at 50 °C with stirring for 4 h and then cooled to room temperature and filtered. Slow diffusion of diethyl ether into the filtrate of the product resulted in the formation of dark orange crystals in 83% yield, which were air dried. UV−vis (solid state in nujol): €νmax 256, 368, 476 nm; FT−IR (ATR κmax/cm−1): 3104, 2860, 1633, 1438, 1329, 1285, 1243, 1030, 965, 903, 877, 844, 772, 571, 521, 488; ESI−HRMS (positive−ion detection, CH2CN): m/z = 543.5168 [Fe + L]+ and 574.0453 [Fe + L + BF4−]. Single crystals were taken from the same sample and used directly for the X-ray study.

■ ASSOCIATED CONTENT

 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00630.

Crystallographic data (CIF) (CIF) (CIF)

Additional experimental details on the characterization and physical property measurements of ligand L and [FeL](BF4)2 (PDF)

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Notes

The authors declare no competing financial interest.

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