Pressure effects and Mössbauer spectroscopic studies on a 3D mixed-valence iron spin-crossover complex with NiAs topology†

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A three-dimensional mixed-valence iron complex with NiAs-type topology, $[(Fe^{III}_3O)Fe^{II}(TA)_6(H_2O)_3] \cdot (ClO_4)_2(NO_3)(EtOH)(H_2O)_2$ (1, HTA = tetrazole-1H-acetic acid), shows spin-crossover behavior that was characterized via variable-temperature crystal structures, Mössbauer spectra and magnetic susceptibilities, the pressure effects on the transition behavior were also studied.

Spin-crossover (SCO) complexes are interesting bistable systems that contains $3d^{4-7}$ metal ions whose structural, optical and magnetic properties change dramatically between high and low spin states, and can be controlled by external stimuli such as heat, light, magnetic field and pressure.[1] Hence they are promising multifunctional materials as molecular sensors, molecular switches, data storage and other electronic devices.[2] Up to now, numerous spin-crossover complexes with 0D to 3D structures have been reported,[1b,3] and of the ions showing spin-crossover behavior the most examples are found for Fe^{II} with configuration $3d^6$, whose magnetic susceptibility ($\chi_M T$) theoretically varies between 4.90 cm^3 K mol^{-1} ($g = 2.0$) and 0 cm^3 K mol^{-1} and Fe–N distances alter in a range of 0.15–0.20 Å. Because structural information is essential in identifying spin-crossover behavior, it is therefore important to directly measure the Fe–N bond lengths at various temperatures. We report herein a three-dimensional mixed-valence iron complex, $[(Fe^{III}_3O)Fe^{II}(TA)_6(H_2O)_3] \cdot (ClO_4)_2(NO_3)(EtOH)(H_2O)_2$ (1), whose variable-temperature crystal structures along with pressure effects on the magnetic properties and Mössbauer spectra indicate distinct spin crossover behavior.

An ethanol solution (10 mL) containing HTA (36 mg, 0.3 mmol) was layered upon an aqueous solution (1 mL) containing $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ (39 mg, 0.1 mmol), $Gd(NO_3)_3$ or $Nd(NO_3)_3$ (1 mol L^{-1}, 0.1 mL) and $NaClO_4$ (14 mg, 0.1 mmol) (3 : 1 : 1 : 1) in a test tube, orange–red polyhedral crystals of 1 were collected in two weeks, washed with water and dried in

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air (yield: 38% based on HTA). Rare-earth salts were essential in the synthetic process although their effects were not yet clear. A strong peak at 1103 cm^{-1} in the IR spectra indicates the presence of perchlorate anion, the peaks at 1396 and 814 cm^{-1} are assigned to the ν(N–O) modes of nitrate anion, while absorptions at 578 and 692 cm^{-1} are Fe^{III}_3O stretching bands. Thermogravimetry indicates complex 1 releases guest water and ethanol molecules up to 240 °C, then the framework begins to decompose above 240 °C along with the release of coordinated water, the uncoordinated nitrate and perchlorate anions, and the decomposed TA ligands.

Single-crystal X-ray diffraction data of 1 were collected at 90, 150, 210, 270 and 330 K, respectively.‡ No structural transition was observed in this temperature range. An ORTEP drawing (270 K) of the basic unit is shown in Fig. 1(a). The structure contains trinuclear $[(Fe_3O)(OOC)_6(H_2O)_3]$ moieties that are connected to Fe^{II} ions through the $\kappa^1,\kappa^1,\kappa^1,\mu_3$-tetrazole-1H-acetate ligands. For a trinuclear Fe_3O unit in a molecule with crystallographic threefold symmetry, the Fe–μ_3-O distance is usually temperature-independent and about 1.9 Å.[4] In the case of 1, the Fe2–μ_3-O1 distance is 1.893(6) Å at 270 K and nearly constant in all the temperature range, except that at 330 K it is a little longer than those at lower temperature. So, it can be concluded that the Fe_3O unit is an isovalent Fe^{III} unit, and not a mixed-valence one. The Fe1 ion is located in octahedral coordination geometry formed with six N1 atoms from six TA ligands. If the carboxylate-bound Fe_3O moiety as regarded as a prismatic unit and the FeN_6 moiety as an octahedral unit, the three-dimensional structure can then be regarded as a NiAs-type framework[5] (Fig. 1(b)), in which voids are occupied by disordered perchlorate and nitrate anions, guest ethanol and water molecules. It should be noticed that only one metal–organic complex with NiAs-type structure has ever been reported[6] although researchers have synthesized numerous metal–organic complexes with various topologies.
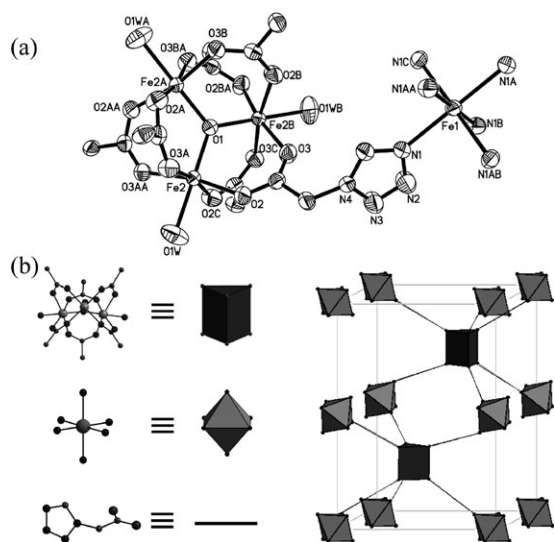
A temperature-difference map[7] (150/90 K, Fig. 2(a)) calculated with coefficients $F_o(150 \text{ K}) - F_o(90 \text{ K})$ clearly shows the movement of tetrazole ring that reflects the Fe1–N bond distances are obviously temperature-dependent. From the structural data (Table 1), the Fe1–N distances are 2.011(2) Å at 90 K and 2.198(3) Å at 330 K, respectively, the latter is longer than the former by 0.187 Å due to that the fraction of high-spin (hs) Fe^{II} ions increases with increasing temperature, unambiguously indicating spin-state crossover. DFT calculation[8] based on a hypothetical $\{Fe^{II}(N_4CH\text{-}CH_3)_6\}$ unit shows

Fig. 1 (a) ORTEP drawing at 30% probability of the structural fragment of **1** with atom labels. (b) The three-dimensional NiAs-type structure of **1** constructed from prismatic and octahedral building blocks.

that Fe1–N distances are 2.208 and 2.019 Å at high- and low-spin (ls) states, respectively. As shown in Table 1, the measured Fe1–N distances at 90 and 330 K are close to the theoretical values and a little longer than those found for low- and high-spin Fe^{II} complexes, respectively.[3,9] The cell volume increases by 6.4% from 90 to 330 K, which is also larger than those found for normal Fe^{II} spin-crossover complexes.[3,9] It can also be concluded from Table 1 that most of spin crossover in **1** takes place in the temperature range of 90–210 K.

The magnetic data in the form of $\chi_M T$ vs. T at different pressures with an applied field of 5 kOe are shown in Fig. 2(b) (based on the Fe_4 unit). Under no additional pressure, the $\chi_M T$ value is 8.53 cm^3 K mol^{-1} at 300 K, which decreases with decreasing temperature in a nearly sigmoidal shape and reaches a value of 2.45 cm^3 K mol^{-1} at 9 K, then a second decrease is observed, which may correspond to the zero-field splitting of the Fe^{III} centers. Due to the antiferromagnetic property of the trinuclear $\{Fe^{III}_3O\}$ unit, it is difficult to figure out whether Fe1 undergoes an abrupt spin crossover. Most possibly, the spin crossover gradually took place. The crossover temperature is between 150 and 210 K for both the cooling and warming modes without any hysteresis. When pressure is added to 4.97 kbar, the $\chi_M T$ value is 6.99 cm^3 K mol^{-1} at 300 K, lower than that observed without additional pressure, which indicates that a small amount of molecules transform into the ls state. The $\chi_M T$ value also gradually diminishes with decreasing temperature at this pressure. Furthermore, it is interesting that a narrow reproducible hysteresis ($T_{SC\downarrow}$ = 163 K and $T_{SC\uparrow}$ = 170 K) occurs under this pressure. Increasing pressure up to 6.01 kbar causes the disappearance of hysteresis and an evident shift of T_{SC} upwards to 210 K. Further increase of pressure up to 8.15 and 11.56 kbar causes the plateau in the high-temperature range to disappear, and moreover, the Fe1 center is believed to be completely in the ls state at 300 K and 11.56 kbar according to the $\chi_M T$ value (3.43 cm^3 K mol^{-1}).
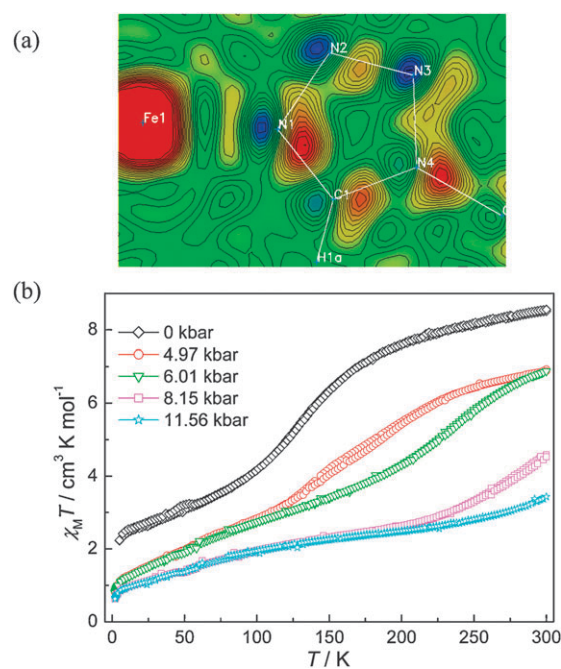
Fig. 2 (a) The temperature-difference (150/90 K) map shows the movement of tetrazole ring (isosurfaces at ±0.01). (b) Magnetic susceptibilities (1 K min^{-1}) of **1** measured at 0, 4.97, 6.01, 8.15 and 11.56 kbar under an applied field of 5 kOe.

Evidently, pressure effects on the SCO behavior of complex **1** were observed, the temperature of T_{SC} increases gradually with increasing pressure. Moreover, the hysteresis appears at a critical pressure, but vanishes at any other pressure conditions. It may be concluded that a nonlinear hysteretic behavior of $T_{SC}(P)$ vs. P was observed in **1**. It is well-known that most SCO systems follow linear dependence of $T_{SC}(P)$ vs. P,[10] and the mean-field theory of phase transitions in SCO complexes predicts a decrease of the hysteresis width with increasing pressure.[11] On the other hand, the nonlinear hysteretic behavior of $T_{SC}(P)$ vs. P has also been observed in some SCO compounds.[9a,12]

In order to further confirm the spin-crossover behavior of complex **1**, ^{57}Fe Mössbauer spectra were measured in the cooling mode as shown in Fig. 3. At room temperature, two quadrupole doublets were observed, which were fitted by Lorentzian line shape, one with isomer shift (IS) value 0.77 mm s^{-1} and quadrupole splitting (ΔE_Q) value 1.63 mm s^{-1} assigned to high-spin Fe^{II} and another one with IS value 0.33 mm s^{-1} and ΔE_Q value 0.42 mm s^{-1} assigned to high-spin Fe^{III}. The high-spin Fe^{II} signals decrease with decreasing temperature and vanish at 9 K, which is attributed to the spin crossover of Fe^{II} from high- to low-spin in the temperature range. Moreover, according to the area ratios of quadrupole-split doublets, it can be deduced that only half of high-spin Fe^{II} transformed to low-spin Fe^{II} from 300 to 150 K.

Table 1 Observed and calculated Fe1–N bond distances

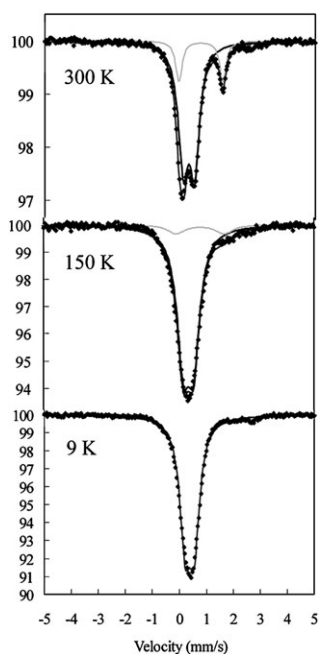| T/K	90	150	210	270	330
Fe1–N (obs.)	2.011	2.050	2.174	2.185	2.198
Fe1–N (calc.)	2.019 (ls)				2.208 (hs)

Fig. 3 Mössbauer spectra of complex **1** at various temperature.

Additionally, Mössbauer spectra exhibit an almost unchangeable unique quadrupole doublet from 300 to 9 K, and its respective IS and ΔE_Q values of 0.33 mm s^{-1} and 0.42 mm s^{-1}, strongly suggesting that all three Fe centers in the trinuclear iron carboxylate unit are identical and at the $+3$ oxidation state. This can be further proved by the 9 K Mössbauer spectra, a doublet with IS value of 0.5–0.7 mm s^{-1} and ΔE_Q value of more than 1 mm s^{-1}, representing 75% of the hs-Fe^{III} (3Fe^{III} + Fe^{II}) in the sample, consistent with the crystal structure of **1**.

In conclusion, a three-dimensional mixed-valence iron framework constructed from trigonal prismatic and octahedral building units featuring NiAs-type topology has been synthesized. Variable-temperature Fe–N distances imply spin-crossover behavior of the tetrazolato-coordinated Fe^{II} ion, which is further confirmed by theoretical calculation, magnetic properties and Mössbauer spectra. Furthermore, the spin crossover behavior of complex **1** is very sensitive to the application of pressure, which may be due to strength changes of the crystal field of the Fe^{II} center.

Notes and references

‡ Elemental analysis (%) for complex **1**: Calc. (found) for C$_{20}$H$_{34}$N$_{25}$O$_{30}$Cl$_2$Fe$_4$: C, 17.17 (17.18); N, 25.03 (25.04); H, 2.45 (2.27). IR (KBr) ν/cm^{-1}: 3436s, 1646s, 1454m, 1396s, 1331w, 1103s, 814w, 692m, 624w, 578w. *Crystal data* for **1**: C$_{20}$H$_{34}$N$_{25}$O$_{30}$Cl$_2$Fe$_4$, M_r = 1398.93 g mol^{-1}, hexagonal, space group $P6_3/m$, Z = 4. At 90(2) K: a = 10.7052(2), c = 22.9656(7) Å, V = 2279.28(9) Å^3, D_c = 1.913 g cm^{-3}, R_1 = 0.0456, wR_2 = 0.1333, μ = 1.484 mm, S = 1.113. At 150(2) K: a = 10.7401(3), c = 23.0238(6) Å, V = 2299.98(9) Å^3, D_c =

1.896 g cm^{-3}, R_1 = 0.0502, wR_2 = 0.1623, μ = 1.471 mm^{-1}, S = 1.144. At 210(2) K: a = 10.8575(2), c = 23.1037(4) Å, V = 2358.69(6) Å^3, D_c = 1.849 g cm^{-3}, R_1 = 0.0509, wR_2 = 0.1829, μ = 1.434 mm^{-1}, S = 1.206. At 270(2) K: a = 10.8858(2), c = 23.1388(5) Å, V = 2374.61(7) Å^3, D_c = 1.836 g cm^{-3}, R_1 = 0.0509, wR_2 = 0.1561, μ = 1.425 mm^{-1}, S = 1.138. At 330(2) K: a = 11.036(6), c = 22.991(15) Å, V = 2425.2(19) Å^3, D_c = 1.798 g cm^{-3}, R_1 = 0.0564, wR_2 = 0.1799, μ = 1.395 mm^{-1}, S = 1.131. X-Ray crystallographic data were collected with a Mo-Kα radiation source (λ = 0.710 73 Å) by using Bruker SMART CCD diffractometer equipped with graphite monochromator. The structures were solved by direct methods and refined by full-matrix least-squares calculations (F^2) by using the SHELXTL-97 software. All non-H atoms were refined in the anisotropic approximation against F^2 for all reflections. All H atoms were placed at their calculated positions and refined in the isotropic approximation. The distorted nitrate ion (1/6 per unit), ethanol (1/6 per unit) and water molecules in the asymmetric structural unit were treated as disordered oxygen (water) atoms, the molecular formula was confirmed by elemental analysis. CCDC 668963–668967. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b718456e.

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