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The biferrocene-based salt $[\text{Bifc}]_2[\text{Ni}(\text{mnt})_2]_3$ (Bifc = bis(isopropylthio)-biferrocene; mnt = maleonitriledithiolate) contains a biferrocenium monocation and dication within the same crystal. The coexistence of Fe^{3+} and mixed-valence $\text{Fe}^{2.5+}$, which resembles the valence state of magnetite, was confirmed by Mössbauer spectroscopy.

Magnetite (Fe_3O_4) is a basic mixed-valence compound that has attracted significant attention.¹ In the inverse spinel structure of magnetite, the tetrahedral sites (A sites) and octahedral sites (B sites) are occupied by Fe^{3+} ions and $\text{Fe}^{2.5+}$ ions, respectively, and the latter ions comprise Fe^{2+} and Fe^{3+} ions that undergo rapid electron exchange, as demonstrated by ^{57}Fe Mössbauer spectroscopy and other methods.^{1,2} Mixed valency in molecular compounds and metal complexes has attracted considerable interest.^{3,4} Biferrocenium salts are well-known organometallic mixed-valence compounds.⁵ Biferrocenes exhibit three redox states, *i.e.*, neutral, monocation, and dication (Fig. 1), and produce salts with mixed-valence monocations. We previously reported a biferrocenium salt that undergoes a phase transition from a monocationic to dicationic salt at low temperatures, which demonstrates that the dicationic species can exist when stabilized by electrostatic interactions.⁶ Herein, we report the intriguing valence state of a biferrocene-based salt, *i.e.*, $[\text{Bifc}]_2[\text{M}(\text{mnt})_2]_3$ (**1**, Bifc = 1',1''-bis(isopropylthio)-1,1''-biferrocene, Fig. 2) that exhibits a 2:3 cation/anion ratio and contains both a mixed-valence monocation and dication in the same crystal.[‡] $[\text{Ni}(\text{mnt})_2]^-$ is a planar paramagnetic anion, which has produced intriguing ferrocenium-based salts.⁷

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† Electronic supplementary information (ESI) available: Experimental procedures, molecular structures and crystal structures, temperature dependence of ^{57}Fe Mössbauer spectra, and crystallographic data. CCDC 263333 (**1**) and 263334 (**2**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3cc49568j

Biferrocenium salts with magnetite-like mixed-valence iron: coexistence of Fe^{3+} and $\text{Fe}^{2.5+}$ in the crystal[†]

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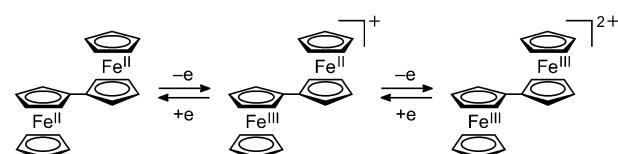


Fig. 1 The three redox states of biferrocene.

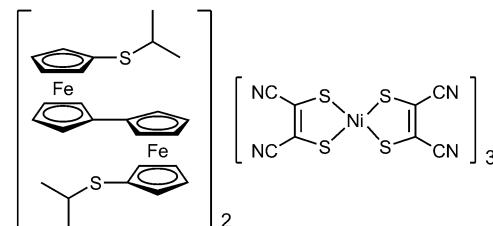


Fig. 2 Chemical formula of $[\text{bis}(\text{isopropylthio})\text{biferrocene}]_2[\text{Ni}(\text{mnt})_2]_3$ (**1**).

The crystal structure of **1** was determined at 173 K (space group $P\bar{1}$).⁸ The packing diagram of **1** viewed along the a -axis is shown in Fig. 3. There are two crystallographically independent cations, *i.e.*, A and B, which are both located on the inversion center. The $[\text{Ni}(\text{mnt})_2]^-$ anions form centrosymmetric trimers, which are further stacked along the a -axis to form a columnar structure (ESI[†]).⁹ The cations are located between the columns of anions. Examination of the intramolecular geometry revealed that cations A and B have different valence states and are dicationic and monocationic, respectively. The average $\text{Fe}-\text{C}(\text{Cp})$ distance in cation A (2.085 Å) is similar to that of a ferrocenium cation (2.08 Å), whereas that in cation B (2.063 Å) is intermediate of that for a ferrocenium cation and neutral ferrocene (2.04 Å) and thus corresponds to a mixed-valence monocation.¹⁰ The valence state of **1** is hence represented as $[\text{Bifc}_A]^{2+}[\text{Bifc}_B]^{+}[\{\text{Ni}(\text{mnt})_2\}_3]^{3-}$. Because the two Fe atoms in each cation are crystallographically equivalent, cations A and B contain Fe^{3+} and averaged-valence $\text{Fe}^{2.5+}$, respectively. The corresponding Pt-containing salt, *i.e.*, $[\text{Bifc}]_2[\text{Pt}(\text{mnt})_2]_3$ **2**, has a similar structure¹¹ and the same valence state characteristics.



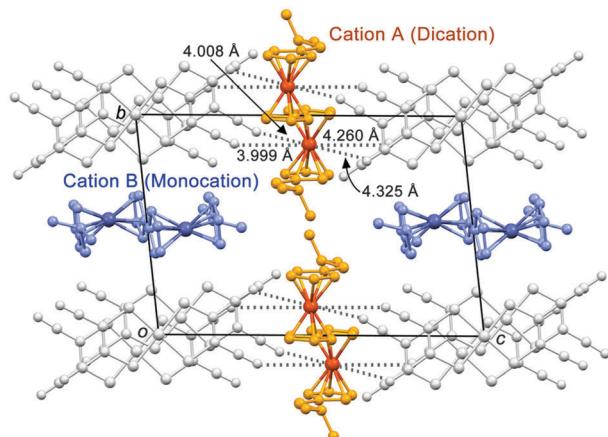


Fig. 3 Packing diagram of **1** viewed along the *a*-axis. Hydrogen atoms are omitted for clarity. Dotted lines indicate the close $\text{Fe}\cdots\text{NC}$ distances between the cation and the anion.

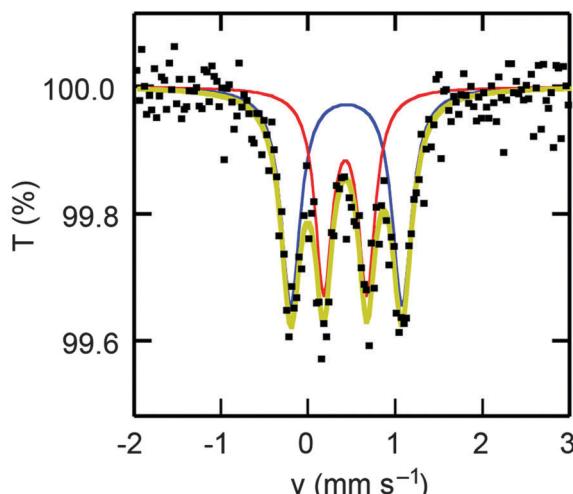


Fig. 4 ^{57}Fe Mössbauer spectrum of **1** recorded at 300 K.

The valence states of the iron atoms in the cations were unambiguously determined using ^{57}Fe Mössbauer spectroscopy. Fig. 4 shows the spectrum recorded at 300 K, which features two equal-intensity components. The inner doublet, which has an isomer shift of 0.43 mm s^{-1} (relative to α -iron) and a quadrupole splitting of 0.49 mm s^{-1} , corresponds to Fe^{3+} in the biferrocenium dication (cation A). The outer doublet, which has an isomer shift of 0.44 mm s^{-1} and a quadrupole splitting of 1.28 mm s^{-1} , corresponds to $\text{Fe}^{2.5+}$ in a mixed-valence biferrocenium monocation that undergoes rapid valence exchange ($>10^8 \text{ s}^{-1}$, cation B).⁵ The spectral features remain unchanged down to 6 K (Fig. S1, ESI[†]).

This salt, which contains Fe^{3+} and $\text{Fe}^{2.5+}$, is isoelectronic to magnetite in terms of the valence state of the iron, while the electron transfer between Fe^{2+} and Fe^{3+} is intramolecular. Although magnetite undergoes a charge-ordering transition at around 119 K,¹ **1** exhibits no valence localization of the $\text{Fe}^{2.5+}$ site, at least down to 6 K; thus, it is highly likely that valence tautomerization of **1** occurs *via* electron tunneling.¹² The origin

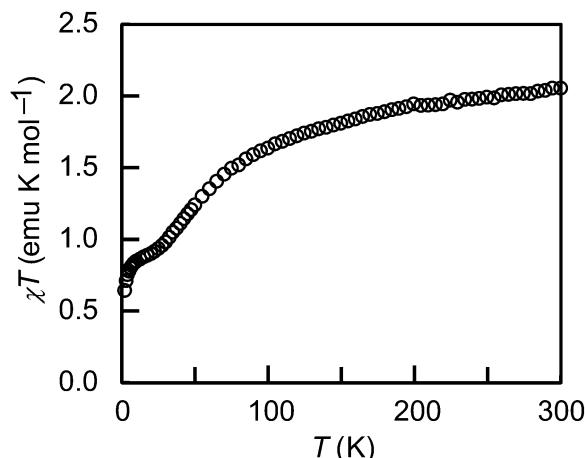


Fig. 5 Temperature dependence of the magnetic susceptibility (χT value) of **1**.

of the coexistence of a dication and monocation in **1** is reasonably attributed to differences in the local electrostatic interactions. The ferrocenium sites in biferrocenium-[Ni(mnt)₂] salts are stabilized by neighboring cyano groups.⁹ In **1**, the Fe atom in cation A is surrounded by four electronegative cyano groups from the anion ($\text{Fe}\cdots\text{NC}$ distances: $3.999(4)$ – $4.325(4)$ Å, indicated by dotted lines in Fig. 3), which strongly stabilizes the cationic state; in contrast, cation B has no such interactions.

This salt exhibits paramagnetic behavior. The temperature dependence of the χT value is shown in Fig. 5. **1** has a magnetic susceptibility of $2.06 \text{ emu K mol}^{-1}$ at room temperature and contains three spins of the ferrocenium cation: two from cation A and one from cation B. The magnetic moment of the ferrocenium cation is 0.6 – $0.7 \text{ emu K mol}^{-1}$, which is larger than the spin-only value because of orbital contributions.⁶ Hence, the total magnetic moment of the cations in **1** is expected to be 1.8 – $2.1 \text{ emu K mol}^{-1}$; this corresponds with the observed value. The contributions of the anion spins are small because of strong antiferromagnetic interactions in the column.^{9,10a} The gradual decrease of the magnetic moment down to about 30 K is ascribed to loss of the orbital contributions; the magnetic moment at this temperature is close to the spin-only value of $3 \times 0.375 = 1.13 \text{ emu K mol}^{-1}$. This temperature-dependent loss of the orbital contribution in biferrocenium salts is exceptional^{5d,6} and likely results from the electronic effects of sulfur.¹³ The susceptibility suddenly decreases at 5 K, which is probably ascribed to singlet formation in the dication (cation A). These magnetic behaviors are consistent with the valence state of the salt.

In summary, we discovered an organometallic compound that contains Fe^{3+} and $\text{Fe}^{2.5+}$ and exhibits a magnetite-like mixed-valence state of the iron ions. Intramolecular charge separation to Fe^{3+} and $\text{Fe}^{2.5+}$ has been observed in a few trinuclear mixed-valence complexes at low temperatures;¹⁴ however, the present example involves intermolecular charge separation, which originates from the different local electronic interactions around each cation. This phenomenon is interesting from the perspective of the recent interest in charge separation in molecular charge-transfer



salts.¹⁵ A somewhat related phenomenon is the inclusion of neutral ferrocene in $[\text{Fe}(\text{C}_5\text{H}_5)_2]_2[\text{Ni}(\text{mnt})_2]_2 \cdot [\text{Fe}(\text{C}_5\text{H}_5)_2]$.^{7a}

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Notes and references

‡ 1',1'''-Bis(isopropylthio)-1,1''-biferrocene was prepared *via* the reaction of dilithioferrocene and diisopropyl disulfide in hexane (ESI†). The cyclic voltammogram of this molecule showed two reversible redox waves at $E_{(1)}^{1/2} = -0.07$ V and $E_{(2)}^{1/2} = 0.22$ V (vs. $[\text{Fe}(\text{Cp})_2]^{0/+}$), which are similar to those of biferrocene, *i.e.*, $E_{(1)}^{1/2} = -0.10$ V, $E_{(2)}^{1/2} = 0.24$ V. Single crystals of **1** were obtained as black plates in an ~40% yield by vapor diffusion of pentane into a dichloromethane solution of equimolar amounts of biferrocene and $[\text{Fe}(\text{C}_5\text{H}_5)_2]_2[\text{Ni}(\text{mnt})_2]$. Anal. calcd for $\text{C}_{76}\text{H}_{60}\text{S}_{16}\text{N}_{12}\text{Fe}_4\text{Ni}_3$: C, 44.44; H, 2.94; N, 8.18%. Found: C, 44.15; H, 3.03; N, 8.04%.

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- 8 Crystallographic parameters for **1** at 173 K: triclinic $P\bar{1}$, $a = 10.4988(14)$ Å, $b = 12.0318(16)$ Å, $c = 17.227(2)$ Å, $\alpha = 95.436(3)$ °, $\beta = 92.971(3)$ °, $\gamma = 103.641(3)$ °, $V = 2099.0(5)$ Å³, $Z = 1$, $R_1 = 0.0536$, and $wR_2 = 0.1317$. See ESI† for details. The crystal structure at 295 K was unchanged from that at 173 K.
- 9 $[\text{Ni}(\text{mnt})]$ in **1** is monoanionic, as evidenced by the infrared CN stretching band ($\nu_{\text{CN}} = 2207$ cm^{−1}) and intramolecular geometry (Ni–S bond lengths: 2.138(1)–2.153(1) Å).⁹ The intratrimer and intertrimer Ni···Ni distances are 3.94 Å and 4.35 Å, respectively. The intratrimer and intertrimer overlap integrals between the SOMOs of the anions calculated using the extended Hückel method are 4.8×10^{-3} and 11.4×10^{-3} , respectively.
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- 11 Crystallographic parameters for **2** at 173 K: triclinic $P\bar{1}$, $a = 11.084(2)$ Å, $b = 12.270(3)$ Å, $c = 17.696(3)$ Å, $\alpha = 100.459(4)$ °, $\beta = 99.486(4)$ °, $\gamma = 112.620(4)$ °, $V = 2110.4(7)$ Å³, $Z = 1$, $R_1 = 0.0625$, and $wR_2 = 0.1284$. The crystal structure at 295 K was unchanged from that at 173 K. The intratrimer and intertrimer Pt···Pt distances are 3.77 Å and 5.68 Å, respectively. See ESI† for details.
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