CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.201300186

Crystal Structures and Phase-Transition Dynamics of Cobaltocenium Salts with Bis(perfluoroalkylsulfonyl)amide Anions: Remarkable Odd–Even Effect of the Fluorocarbon Chains in the Anion

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Abstract: Crystal structures and thermal properties of cobaltocenium salts with bis(perfluoroalkylsulfonyl)amide $(C_nF_{2n+1}SO_2)_2N$ anions [$n=0$ (**1**), 1 (**1a**), 2 (**1b**), 3 (**1c**), and 4 (**1d**)] and the 1,1,2,2,3,3-hexafluoropropane-1,3-disulfonylamide anion (**2**) were investigated. In these solids, the cations are surrounded by four anions around their C_5 axis, and stacking of these local structures forms two kinds of assembled structures. In the salts with even n (**1**, **1b**, and **1d**), the cation and anion are arranged alternately to form mixed-stack columns in the crystal. In contrast, in the salts with odd n (**1a** and **1c**), the cations and anions independently form segregated-stack columns. An odd–even effect was also observed in the sum of the phase-change entropies from crystal to melt. All of the salts exhibited phase transitions in the solid state. The phase transitions to the lowest-temperature phase in **1**, **1a**, and **2** are accompanied by order–disorder of the anions and symmetry lowering of the space group, which results in the formation of an ion pair. Solid-state ^{13}C NMR measurements on **1a** and **1b** revealed enhanced molecular motions of the cation in the higher-temperature phases.

Keywords: anions · ionic liquids · metallocenes · phase transitions · solid-state structures

Introduction

Ionic liquids are salts with melting points below 100 °C, and their physicochemical properties have been investigated extensively in recent years.[1] Most ionic liquids contain onium cations, but ionic liquids with metal-containing cations are also known.[2] As counteranion, bis(perfluoroalkylsulfonyl)-amide anions $(C_nF_{2n+1}SO_2)_2N$, in particular that with $n=1$ (abbreviated as Tf_2N), are often used because they are more effective in lowering the melting point of the salt than other anions.[1a–c,3] The melting points are determined by the free-energy relationship between the liquid and solid phases, which is affected by intermolecular interactions and dynamics in the solid state. Hence, to understand the origin of the low melting points, elucidation of the thermodynamic and structural characteristics of their salts in the solid state is important.[4,5]

It is known that the melting points and melting entropies of molecular crystals such as *n*-alkanes exhibit odd–even effects with respect to the number of carbon atoms in the alkyl chain, which originate from the different packings of odd-chain and even-chain compounds.[6] In salts relevant to ionic liquids, such effects have been observed in the thermal properties of imidazolium salts with long alkyl chains[7] and in the structures of imidazolium-related salts.[8] However, little has been reported on the anion chain dependence of the thermal properties and structures of the ionic liquids with bis(perfluoroalkylsulfonyl)amide anions.[3a,9,10]

Recently, we reported that alkyl metallocenium salts with bis(perfluoroalkylsulfonyl)amide anions become ionic liquids,[11] whereas the corresponding cobaltocenium salts are solids at room temperature.[11a] We thought that these solids are suitable for structural investigations to elucidate the thermodynamic features of the key anions. This article discusses the thermal properties and crystal structures of cobaltocenium salts with the bis(perfluoroalkylsulfonyl)amide anions $(C_nF_{2n+1}SO_2)_2N$ [$n=0$ (**1**), 1 (**1a**), 2 (**1b**), 3 (**1c**), and 4 (**1d**)] and the 1,1,2,2,3,3-hexafluoropropane-1,3-disulfonylamide anion (**2**), which are shown in Figure 1. The preparation and properties of **1a–d** and **2** were reported previously,[11a] whereas **1** was newly prepared in this study. In the present study, a remarkable odd–even effect with respect to the anion chain length was found in the structures and thermal properties of the solids. We also used solid-state ^{13}C NMR spectroscopy to investigate molecular motions in

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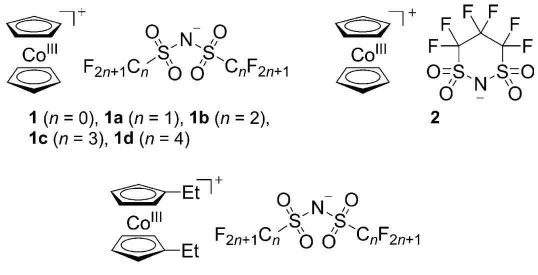
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201300186.



1 (n = 0), **1a** (n = 1), **1b** (n = 2), **1c** (n = 3), **1d** (n = 4)

2

3a (n = 1), **3b** (n = 2), **3c** (n = 3), **3d** (n = 4)

Figure 1. Structural formulas of the cobaltocenium salts investigated in this study.

these solids, because phase transitions in metallocenium salts often accompany changes in molecular motion.[12]

Results and Discussion

Thermal properties: Salt **1** melted at 274.3 °C with accompanying decomposition. The melting point was remarkably higher than those of **1a**–**d**, which are in the range 138–192 °C. Differential scanning calorimetry (DSC) measurements revealed that **1** exhibits phase transitions at −43.7, 63.9, and 155.6 °C, accompanied by entropy changes of 21.0, 9.6, and 8.0 J K^{-1} mol^{-1}, respectively. The DSC data for **1a**–**d** and **2** have been reported previously.[11a] The phase sequences for these salts are shown in Figure 2. All of the salts exhibited phase transitions in the solid state, whereby the lowest-temperature phases are designated as phase I. The sums of the entropies of melting and crystal–crystal phase transitions (ΔS_{total}) for **1a**–**d** and relevant ionic liquids **3a**–**d**[12a] (Figure 1) are shown in Figure 3. The data show a remarkable odd–even effect with respect to the carbon number n in the fluorocarbon chain of the anion. Such an odd–even effect in ΔS_{total} has been also observed in normal alkanes,[6] fluoroalkanes,[13] and mesogenic compounds with alkyl chains.[14] The increases observed from **1a** (n=1) to **1c** (n=3) and from **1b** (n=2) to **1d** (n=4) are comparable (15–20 J K^{-1} mol^{-1}); in each case, the change is due to the addition of four difluoromethylene groups. Compounds **3a**–**d** also exhibited the same tendency. These increases are smaller than expected, considering that ΔS_{total} in alkyl imidazolium and alkyl ferrocenium ionic liquids increases by 6–10 J K^{-1} mol^{-1} per methylene group[15] and even higher entropy is expected for difluoromethylene groups.[16] This is probably because the chains are short, and a similar phenomenon has been also observed in alkyl imidazolium ionic liquids.[15b]

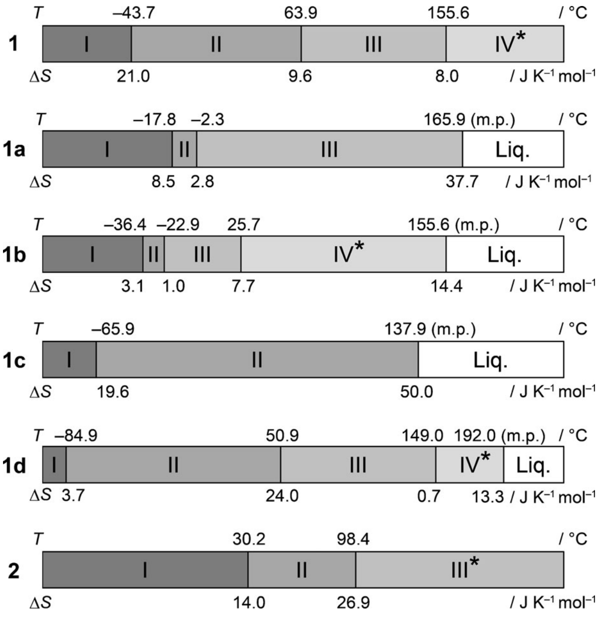


Figure 2. Phase sequences of **1**, **1a**–**d**, and **2**. The transition temperatures [°C] and transition entropies [J K^{-1} mol^{-1}] are shown. Highly disordered phases are indicated by an asterisk.

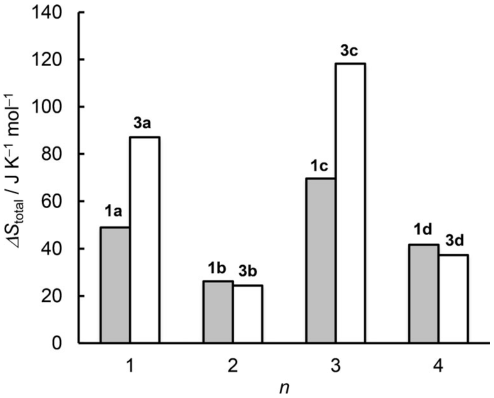


Figure 3. Total phase change entropies ΔS_{total} of **1a**–**d** and **3a**–**d** plotted against the carbon number n in the anion $(C_nF_{2n+1}SO_2)_2N$.

Among **1** and **1a**–**d**, the salts with even n (**1**, **1b**, and **1d**) commonly exhibited three phase transitions in the solid state. The small melting entropies of the highest-temperature phases (phase IV) in **1b** and **1d** (14.4 and 13.3 J K^{-1} mol^{-1}, respectively) indicate that these phases are highly disordered. Although the molecules in the highest-temperature phase of **1b** were found to undergo anisotropic rotation (see below), they can be regarded as ionic plastic phases[17] having melting entropies smaller than 20 J K^{-1} mol^{-1}.[18] It is plausible that the highest-temperature phases in **1** and **2** are also highly disordered, considering their molecular shape and the phase sequences. In contrast, the salts with odd n (**1a** and **1c**) exhibited fewer phase transitions and large melting entropies, which suggest less disorder in these solids.

Structural odd–even effects: In this section, the general features of the crystal structures of **1** and **1a**–**d** and their correlation with the thermal properties are discussed. In these salts, each cation is surrounded by four anions around its C_5 axis (Figure 4 a), except that **1c** has three neighboring anions. This unit is stacked to form two kinds of assembled structures (Figure 4 b) depending on the carbon number n in the anion, with a remarkable odd–even effect. The salts with even n (**1**, **1b**, and **1d**) adopt mixed-column structures, in

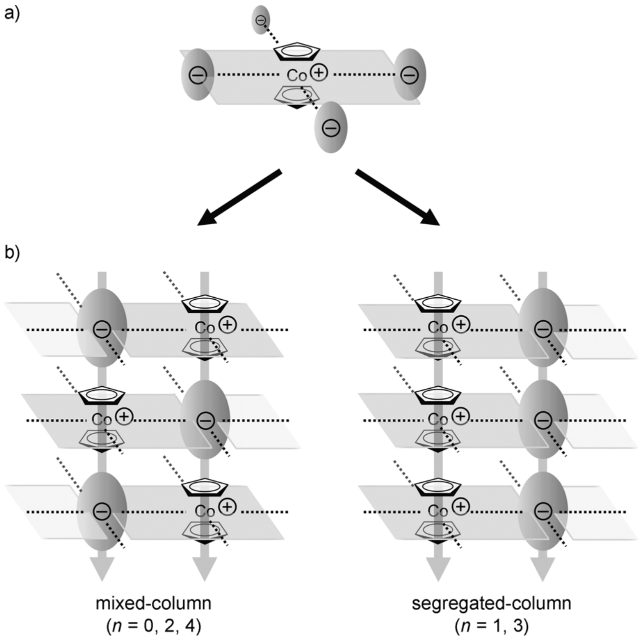


Figure 4. Schematic illustration of the assembled structures of the cations and anions in **1** and **1a–d**. a) The primary structure formed by the cation–anion interactions around the C_5 axes of the cation. b) Two types of secondary structures formed by stacking of the primary structures.

which the anions and cations are arranged alternately, whereas the salts with odd n (**1a** and **1c**) adopt segregated-column structures. The X-ray structures of the anions in **1** and **1a–d** and their neighboring molecules in the columns are shown in Figure 5. All of the anions adopted the *trans* (C2) conformation (Figure 5), in which the two fluoroalkyl groups are on the opposite sides of the central S-N-S plane. This conformation is more stable than the *cis* (C1) conformation and more often found in the solid state.[5,19] The conformations of the fluoroalkyl chains are mostly all-*trans*, whereas the torsion angles in the chain deviate slightly from 180° because of steric repulsion between the fluorine atoms.[20] Because the odd–even effect in n-alkanes originates from the influence of the terminal CH_3 groups on their crystal packing,[6] the end-group effect may be also important in the present salts. For the anions with even n (Figure 5a), the terminal CF_3 groups face the cyclopentadienyl (Cp) rings of the cation to form the mixed-column structure. This configuration is unfavorable for the anions with odd n, because their terminal CF_3 groups are directed outward from the molecular long axes, as is indeed found in **1a** and **1c** (Figure 5b).

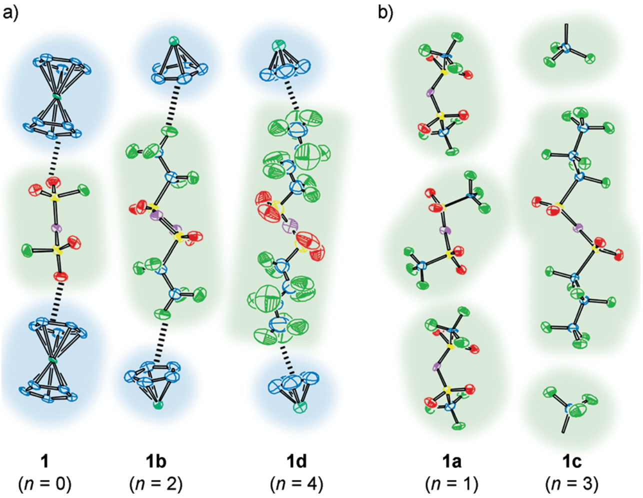


Figure 5. The molecular arrangements around the anions in the columnar structures in the a) mixed-column salts (**1**, **1b**, and **1d**) and b) segregated-column salts (**1a** and **1c**). The molecular structure of **1d** in phase II and those of the other compounds in phase I are shown. Dashed lines indicate cation–anion contacts.

The odd–even effect observed in ΔS_{total} should be ascribed to the odd–even effect in the structure. In n-alkanes, compounds with even numbers of carbon atoms have higher densities and exhibit larger ΔS_{total} than those with odd ones.[6] The harder crystal lattice due to the higher density leads to smaller entropy gain through thermal excitation of lattice vibrations and larger entropy gain through phase transitions. Therefore, in the present salts, the larger ΔS_{total} in the segregated-column salts may be due to their possible denser crystal packing, likely resulting from interlocking of the terminal CF_3 groups between the anions in the column. This seems to hold for **1c**, the density of which was large as determined crystallographically, but the density of **1a** was comparable to those of the others and hence this point is not clear. The comparison of ΔS_{total}, which virtually corresponds to the entropy of transition from the ordered crystals to liquids, is not strict, because **1b** has some disorder in phase I (see below), but this does not affect the overall tendency. Concerning the high temperature phases, it seems reasonable that the mixed-column structures exhibited ionic plastic phases at high temperatures, because each ion is symmetrically surrounded by oppositely charged ions in the structure. The absence of such phases in the segregated-column salts may be consistent with their heterogeneous local crystal environment.

The structure of **2** consists of the same structural unit as seen in **1** and **1a–d**, in which four anions surround the cation. The assembled structure, however, is neither the mixed-column structure nor the segregated-column structure, and is more isotropic due to the ring shape of the anion.

Structural changes through phase transitions: The crystal structures in phases I and II were determined for all salts except for **1c**, and this allowed elucidation of the structural changes through the phase transitions. The transitions in **1**, **1a**, and **2** are accompanied by order–disorder of the anions and exhibit large transition entropies (21.0, 8.5, and 14.0 $J\,K^{-1}mol^{-1}$ for **1**, **1a**, and **2**, respectively). In contrast, the order–disorder of the anions in **1b** and **1d** is unchanged in phases I and II, which is consistent with their small transition entropies (3.1 and 3.7 $J\,K^{-1}mol^{-1}$, respectively).

In **1**, **1a**, and **2**, the central nitrogen atom (-S-N-S-) in the anion is disordered over two sites in phase II, as is found in several Tf_2N salts,[5b] whereas the anions are ordered in phase I and form ion pairs with the neighboring cation. These transitions accompany symmetry lowering of the crystal lattice. The change of the local crystal environment is shown below. In these salts, one cation is surrounded by four anions around its C_5 axis (Figure 4a). For example, the arrangements of the anions around the cation in **1** in phases I and II are shown in Figure 6. In this salt, the cation has the same distances to the four neighboring anions in phase II (Co···N 4.83 Å) owing to the higher crystal symmetry and anion disorder (Figure 6a). In phase I, however, one of the nitrogen atoms of the anions comes closer to the cation to form a cation–anion pair (Co···N distance: 4.60 Å), associated with ordering of the nitrogen atom (Figure 6b). In the bis(perfluoroalkylsulfonyl)amide anions, the central nitrogen atom is the most negatively charged. Hence, it is reasonable to regard this as ion pairing considering the long-range nature of the Coulombic force. The other anions are close to the Co ion at the oxygen atoms. The molecular arrangements around the cation in the other salts are shown in Figure S1 (Supporting Information). The phase transitions in **1a** and **2** closely resemble that in **1** in terms of the order–disorder of the anion and the resultant ion pairing. In contrast, anion order–disorder in **1b** and **1d** are unchanged in phases I and II. In both phases, **1b** contains two disordered anions and one ordered anion, whereas **1d** contains only ordered anions that form ion pairs.

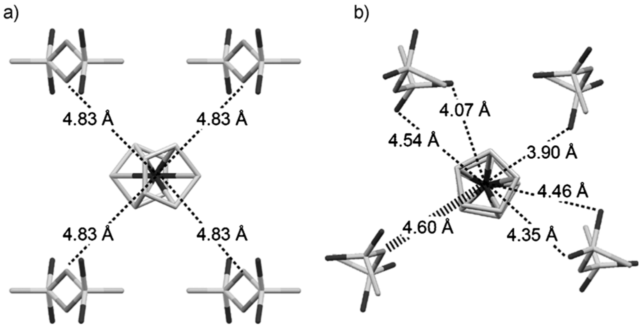


Figure 6. Molecular arrangements around the cation of **1** in a) phase II and b) phase I. Dotted lines show Co···X (X = O, N) distances shorter than 5 Å. The Co···N ion-pair-like interaction in b) is indicated by a thicker dotted line.

The Co···X distances (X = N, O) between the cation and anion in these salts are longer than the van der Waals contact distances, but the CH···X distances in **1a–d** are shorter than the van der Waals contact distances by about 0.3 Å, which probably results from the cation–anion electrostatic interactions. Such weak intermolecular CH···X interactions are often observed in the crystal structures of ionic liquids with bis(perfluoroalkylsulfonyl)amide anions.[4,10] There are no such CH···X contacts in **2**. Conformational changes of the related anions at phase transitions have been discussed for several onium salts.[5] This study has revealed a strong tendency for disorder of the anions and their ordering accompanying ion-pair formation in the low temperature phases.

The structural features of each salt in phases I and II are described in the following sections. Structure determinations on the higher-temperature phases were unsuccessful.

Crystal structures of salts with even *n*: Salts **1**, **1b**, and **1d** exhibit mixed-column structures. The packing diagrams of **1** in phases I and II are shown in Figure 7a. The space group changed from monoclinic $C2/m$ (phase II) to triclinic $P\bar{1}$ (phase I). The unit cells were much changed at the phase transition, whereas the cell volumes were comparable. In phase II, the cations and anions in the unit cell are located at the vertices and face-centered positions, respectively (Figure 7a, upper). The Cp ring of the cation contacts the SO_2F group of the anion, which forms an alternate column extending along the *ac* direction. The central nitrogen atom of the anion was disordered over two sites with equal occupancies and the SO_2F groups exhibit rotational disorder. A layer structure in which one cation is surrounded by four anions and vice versa is formed in the *bc* plane, and, as discussed above (Figure 6), one of the four anions forms an ion pair with the cation in phase I associated with ordering of the anion. The cation–anion arrangement in phase I is slightly altered from that in phase II and deviates from an ideal mixed-column structure.

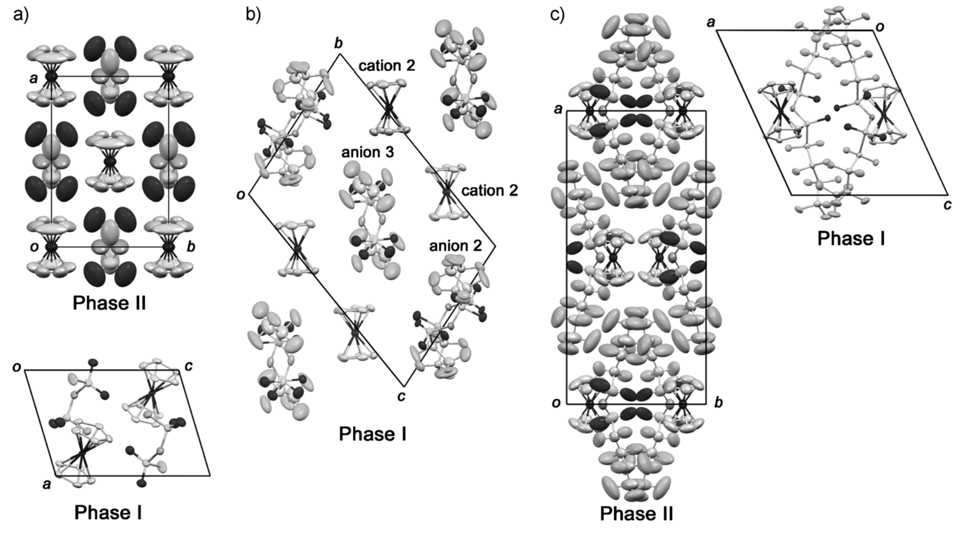


Figure 7. Packing diagrams of a) **1** in phase II (top) and phase I (bottom), b) **1b** in phase I, and c) **1d** in phase II (left) and phase I (right). In b), only cation 2 and anions 2 and 3 are shown for simplicity. The hydrogen atoms have been omitted for clarity.

The packing diagram of **1b** in phase I is shown in Figure 7b. The unit-cell dimensions, space groups (triclinic $P\bar{1}$), and the molecular arrangements are almost the same in phases II and I. The crystal structure is more complicated than those of the other salts. The asymmetric unit contains two cations (cations 1 and 2), one ordered anion (anion 1), and two disordered anions (anions 2 and 3), and half the molecules are independent. In the disordered anions, both the nitrogen and oxygen atoms are disordered over two sites, and the pentafluoroethyl groups are rotationally disordered. The columns formed by anion 1 and cation 1 are arranged orthogonal to the columns formed by anions 2 and 3 and cation 2. Both cations 1 and 2 are surrounded by four anions (Figure S1b, Supporting Information), forming ion pairs with anions 2 and 1, respectively. Anion 3 forms no ion pair and exhibits larger thermal ellipsoids than the other anions. The unit-cell dimensions in high-temperature phase III are comparable to those of phases I and II. The crystal system in high-temperature phase IV is orthorhombic; hence, the cations and anions may be undergoing anisotropic rotation.

The packing diagrams of **1d** are shown in Figure 7c. The space group changed from monoclinic $C2/c$ (phase II) to triclinic $P\bar{1}$ (phase I). The unit-cell volume in phase I is half of that of phase II, and such a decrease in cell volume in the lower-temperature phase is a rare phenomenon. In both phases, the anion is ordered and the cation is surrounded by four anions around its C_5 axis, similar to **1** (Supporting Information Figure S1d), forming ionic layers on *bc* planes at $x=0$ and 0.5 (Figure 7c, left). There are fluorous layers between them, in which perfluoroalkyl groups contact each other. In phase II, one of the four surrounding anions forms an ion pair with the cation (Co···N 4.62 Å). The anion adopts a symmetrical structure, and the terminal CF_3 groups face the Cp rings of the adjacent cation to form a mixed-column structure extending along the *a* axis in a zigzag manner. In phase I, however, the anion has an unsymmetrical structure in which one of the chains adopts a *gauche* conformation. This chain contacts the Cp rings in the cation through three fluorine atoms of the bent CF_2CF_2 group. In phase III, the crystal symmetry changed to orthorhombic while maintaining the unit-cell dimensions, which suggests that the anion in this phase undergoes rotation along the molecular long axis.

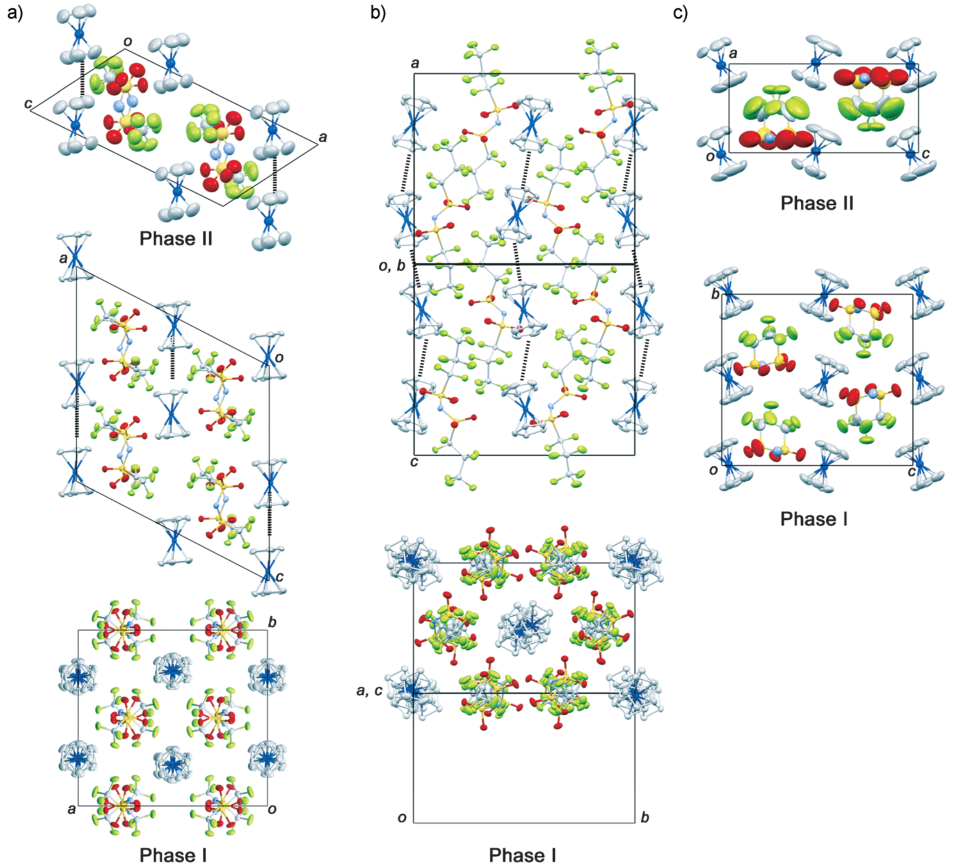


Figure 8. a) Packing diagrams of **1a** in phase II (top) and phase I (middle) projected perpendicular to the column. The bottom figure is a projection along the columns in phase I. b) Packing diagrams of **1c** in phase I, projected along [101] (top) and [10$\bar{1}$] (bottom). c) Packing diagrams of **2** in phase II (top) and phase I (bottom). The hydrogen atoms have been omitted for clarity. The dashed lines connecting the centroids of the neighboring cyclopentadienyl rings in a) and b) are merely guides to the eye.

Crystal structures of the salts with odd *n*: Salts **1a** and **1c** exhibit segregated-column structures. The packing diagrams of **1a** in phases I and II are shown in Figure 8a. The space group changed from monoclinic $C2/m$ (phase II) to $C2/c$ (phase I), accompanied by cell doubling along the column direction. The molecular arrangements are almost the same in both phases. The cation columns and anion columns are extended along the *c* axis in phase I. In the cation column, the cations form dimers through π–π interactions between the Cp rings, and the dimers are separated by voids surrounded by four CF_3 groups of the anions. In the anion column, the $-SO_2CF_2-$ groups contact with each other between the anions. The cation columns are surrounded by four anion columns and vice versa (Figure 8a, bottom). The anion exhibits disorder in phase II, whereby the nitrogen atom and the oxygen atoms are both disordered over two sites, and the trifluoromethyl groups exhibit rotational disorder. Two of the four anions surrounding the cation have equal Co···N distances of 4.78 Å (Figure S1a, Supporting Information), whereas the anion is ordered in phase I and forms an ion pair with a neighboring cation (Co···N 4.51 Å).

The packing diagram of **1c** in phase I is shown in Figure 8b. The structure in phase II could not be determined. The space group of phase I is monoclinic $P2_1/c$, and the anions are ordered. Columnar arrangements of the cations and anions extend along $[10\bar{1}]$. The cation column is surrounded by six anion columns to form a hexagonal-like arrangement (Figure 8b, bottom). The number of anion columns is twice that of the cation columns, which is a consequence of the long anion (Figure S1c, Supporting Information). This salt is exceptional in that the cations are surrounded by three anions. Only one of the two crystallographically independent cations forms an ion pair (Co···N 4.49 Å).

Crystal structure of 2 having a cyclic anion: The crystal structures of **2** in phases I and II are shown in Figure 8c. The space group changed from orthorhombic *Pbcm* (phase II) to *Pbca* (phase I), accompanied by cell doubling along the *a* axis. The structures are more isotropic than those of the other salts due the quasispherical molecular shape of the anion. In phase II, the anion ring exhibits twofold conformational disorder; the nitrogen atom and the central carbon atom in the $CF_2CF_2CF_2$ group are disordered over two sites. The ordered anion in phase I adopts the energetically favorable chair conformation. Two of the four anions surrounding the cation have equal Co···N distances (4.37 Å) in phase II, whereas one of the anions forms an ion pair with a cation in phase I (Co···N 4.25 Å; Figure S1e, supporting information).

Solid-state ^{13}C NMR spectra: The molecular motion of the cobaltocenium cation in **1a** and **1b** was investigated by solid-state ^{13}C NMR spectroscopy. The line widths of the powder ^{13}C NMR spectra of **1a** are 117, 89, and 69 ppm at −40 °C (phase I), −14 °C (phase II), and 21 °C (phase III), respectively (Figure S2a, Supporting Information). The line width in phase I corresponds to that of an ordered cation, and the value is larger than that of neutral ferrocene in a static state (79 ppm).[21] In this phase, the cation undergoes only rotational jump around the C_5 axis. The much decreased line widths in the higher-temperature phases indicate that the cation has additional motions other than the C_5 rotational jump in the high-temperature phases. The spectra in the high-temperature phases were tentatively analyzed on the basis of a model assuming precession of the cation around the C_5 axis,[22] which provided precession angles of 23° and 32° in phases II and III, respectively. In **1b**, the line widths of the spectra are 111, 102, and 88 ppm at −45 °C (phase I), 18 °C (phase III), and 30 °C (phase IV), respectively (Figure S2b, Supporting Information). The same analysis as above provided precession angles of 17° and 24° for phases III and IV, respectively. These results unambiguously indicate that the molecular motions of the cations are gradually enhanced in the higher-temperature phases in both salts, whereas the cations maintain anisotropic rotation even in their highest-temperature phases. Detailed analyses of molecular motion by NMR spectroscopy will be reported in the future.

Conclusion

Cobaltocenium salts with bis(perfluoroalkylsulfonyl)amide anions $(C_nF_{2n+1}SO_2)_2N$ ($n=0$–4) exhibit an odd–even effect in their total phase-change entropies. This phenomenon is ascribed to difference in their assembled structures, similar to the case of *n*-alkanes. These salts exhibit columnar assembled structures; in the salts with even *n*, the anion and cation are arranged alternately in the columns, whereas the cations and anions form independent columns in the salts with odd *n*. These salts, as well as the salt with 1,1,2,2,3,3-hexafluoropropane-1,3-disulfonylamide anion, exhibit successive phase transitions in the solid state. The appearance of ionic plastic phases in the salts with even *n* seems to be consistent with the mixed-column structure. The molecular motions increase in the higher-temperature phases, as revealed by solid-state ^{13}C NMR spectroscopy.

The bis(perfluoroalkylsulfonyl)amide anions are important anions that are frequently used as components of ionic liquids. To understand thermodynamic aspects of their melting, it is important to investigate their behaviors from the crystal to the melt. By focusing on solids with the simple cobaltocenium cation, we could elucidate the effect of the anions on the melting entropies and their structural features in the solid state. These anions show disorder of the central nitrogen atoms, which often induces more uniform and weaker cation–anion interactions by breaking the ion pairs that exist in the lower temperature phases. Modes of molecular motion are further enhanced at higher temperatures. Both factors contribute to the thermodynamic features of salts with these anions. There results should contribute to the understanding of the thermal properties of salts with these and related fluorinated anions. The structural odd–even effects and their consequences are interesting from the viewpoint of crystal engineering.

Experimental Section

General: Compounds **1a–d** and **2** were prepared according to the literature report.[11a] $[CoCp_2]PF_6$ and potassium bis(fluorosulfonyl)amide (K-$[(FSO_2)_2N]$) were purchased from Sigma-Aldrich and Kishida Chemical, respectively. DSC measurements were performed by using a TA Q100 differential scanning calorimeter from −160 to 325 °C at a scan rate of 10 K min^{-1}. Solid-state ^{13}C NMR spectra were recorded on a Tecmag Apollo spectrometer (operating at 75.431 MHz for ^{13}C) equipped with a Doty XC MAS 4 mm probe head. The ^{13}C NMR experiments were performed with the following parameters: a 4.8 ms π/2 pulse, a 55.6 kHz ^{1}H decoupling field, and a 30 s recycle delay.

Preparation of 1a: An aqueous solution of $[CoCp_2]PF_6$ (100 mg, 0.299 mmol) and $K[(FSO_2)_2N]$ (131 mg, 0.598 mmol) was stirred for 30 min and then extracted with dichloromethane. The organic fraction was dried over anhydrous magnesium sulfate and evaporated to dryness. The product was recrystallized from ethanol. Yield: 102 mg (87.9 %).

Table 1. Crystallographic parameters for **1**, **1b**,and **1d**.

	1		**1b**		**1d**	
	Phase I	Phase II	Phase I	Phase II	Phase I	Phase II
empirical formula	$C_{10}H_{10}CoF_2NO_4S_2$		$C_{14}H_{10}CoF_{10}NO_4S_2$		$C_{18}H_{10}CoF_{18}NO_4S_2$	
formula weight	369.24		569.28		769.32	
T [K]	100	298	100	240	100	298
crystal system	triclinic	monoclinic	triclinic	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$C2/m$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$C2/c$
a [Å]	7.316(4)	12.405(5)	10.509(3)	10.693(3)	10.5048(2)	23.100(6)
b [Å]	9.816(5)	8.505(4)	11.936(3)	12.104(3)	10.7338(2)	10.856(3)
c [Å]	9.982(5)	6.584(3)	17.404(7)	17.530(6)	12.205(2)	10.735(3)
α [°]	79.397(7)	90	104.312(5)	104.417(5)	95.765(2)	90
β [°]	71.188(6)	93.943(5)	101.283(5)	101.724(5)	114.221(2)	98.619(3)
γ [°]	73.631(7)	90	104.134(4)	104.743(3)	92.746(2)	90
V [Å^3]	647.6(6)	693.0(5)	1937.6(11)	2037.1(11)	1242.7(4)	2661.7(1)
Z	2	2	4	4	2	4
ρ_{calcd} [g cm^{-3}]	1.894	1.770	1.916	1.856	2.056	1.920
μ [mm^{-1}]	1.682	1.572	1.197	1.160	1.024	0.956
F(000)	372	372	1128	1128	756	1512
reflns collected	2720	1646	9370	9834	5939	6074
independent reflns	2240	655	6815	7089	4280	2344
R(int)	0.0663	0.0157	0.0322	0.0244	0.0133	0.0204
R_1, wR_2 [$I>2\sigma(I)$]	0.0479, 0.1376	0.0814, 0.2371	0.0724, 0.1924	0.0684, 0.1830	0.0295, 0.0909	0.0840, 0.2552
R_1, wR_2 (all data)	0.0565, 0.1484	0.0821, 0.2402	0.0887, 0.2068	0.1106, 0.2144	0.0304, 0.0912	0.0903, 0.2636
GOF on F^2	1.111	1.108	1.032	1.026	1.216	1.075
parameters	182	55	704	703	397	200
$\Delta\rho_{max,min}$ [e Å^{-3}]	0.850, −0.657	0.758, −0.585	3.317, −1.535	0.713, −0.413	0.312, −0.485	0.701, −0.593

M.p. 274.3 °C (DSC, accompanied by decomposition immediately after melting); FTIR (cm^{-1}): 500, 1012, 1218 (SO), 1419 (SO), 1457, 1472; elemental analysis calcd (%) for $C_{10}H_{10}O_4NS_2CoF_2$: C 32.53, H 2.73, N 3.79; found: C 32.98, H 2.76, N 3.90.

X-ray crystallography: X-ray diffraction data for single crystals of **1**, **1a**–**d**, and **2** were collected on a Bruker SMART APEX II Ultra CCD diffractometer with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Crystallographic parameters of the salts are listed in Tables 1 and 2. All calculations were performed with SHELXL.[23] The nonhydrogen atoms were refined anisotropically, and hydrogen atoms were inserted at calculated positions. Empirical absorption corrections (SADABS)[24] were applied. In **1**, the molecules in phase II were disordered, leaving minor electron density peaks ($\Delta\rho < 0.85$ e Å^3) unassigned; the residual electron densities are found around the Cp carbon atoms of the cation and around the central nitrogen atom and the SO_2F groups of the anion. The F and O atoms in the SO_2F groups are disordered, which results in averaged C–X distances (X = F or O). Disorder treatment was unsuccessful due to conversion problems, and the atom assignments in the group are tentative. In **1b**, the CF_2CF_3 groups of the anion are highly disordered, leaving some electron densities unassigned ($\Delta\rho_{max} = 3.32$ e Å^3).

Table 2. Crystallographic parameters for **1a**, **1c**, and **2**.

	1a		**1c**	**2**	
	Phase I	Phase II	Phase I	Phase I	Phase II
empirical formula	$C_{12}H_{10}CoF_6NO_4S_2$		$C_{16}H_{10}CoF_{14}NO_4S_2$	$C_{13}H_{10}CoF_6NO_4S_2$	
formula weight	469.26		669.30	481.27	
T [K]	100	263	100	298	313
crystal system	monoclinic	monoclinic	monoclinic	orthorhombic	orthorhombic
space group	$C2/c$	$C2/m$	$P2_1/c$	$Pbca$	$Pbcm$
a [Å]	16.650(5)	16.632(5)	17.847(3)	14.887(3)	7.298(2)
b [Å]	13.725(4)	14.057(5)	16.269(3)	14.479(3)	15.602(5)
c [Å]	16.484(5)	8.748(5)	16.256(3)	16.172(4)	15.698(5)
α [°]	90	90	90	90	90
β [°]	117.336(3)	120.675(5)	111.743(2)	90	90
γ [°]	90	90	90	90	90
V [Å^3]	3746.4(16)	1759.1(13)	4384.1(13)	3485.8(14)	1787.5(9)
Z	8	4	8	8	4
ρ_{calcd} [g cm^{-3}]	1.863	1.772	2.028	1.834	1.788
μ [mm^{-1}]	1.357	1.291	1.119	1.305	1.273
F(000)	1872	936	2640	1920	960
reflns collected	7905	4219	19724	14996	7847
independent reflns	2955	1611	7340	3079	1652
R(int)	0.0278	0.0297	0.0377	0.0261	0.0211
R_1, wR_2 [$I>2\sigma(I)$]	0.0267, 0.0587	0.0895, 0.2196	0.0349, 0.0846	0.0483, 0.1234	0.0978, 0.2860
R_1, wR_2 (all data)	0.0347, 0.0630	0.1057, 0.2340	0.0443, 0.0883	0.0681, 0.1447	0.1102, 0.3030
GOF on F^2	1.032	1.008	1.069	1.025	1.047
parameters	235	173	685	244	145
$\Delta\rho_{max,min}$ [e Å^{-3}]	0.317, −0.339	1.014, −0.656	0.731, −0.438	0.626, −0.611	1.029, −0.641

The packing diagrams were drawn with ORTEP-3[25] and Mercury.[26] CCDC 902768 (**1**, 100 K), 902769 (**1**, 298 K), 902770 (**1a**, 100 K), 902771 (**1a**, 298 K), 902772 (**1b**, 100 K), 902773 (**1b**, 298 K), 902774 (**1c**, 100 K), 902775 (**1d**, 100 K), 902776 (**1d**, 298 K), 915718 (**2**, 298 K), and 915719 (**2**, 313 K) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

We thank Dr. Y. Furuie (Kobe University) for elemental analysis and M. Nakama (Crayonsoft Inc.) for providing a Web-DB system. This work was financially supported by a Grant-in-Aid for Scientific Research (No. 24350073) from the Japan Society for the Promotion of Science.

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Received: January 18, 2013