

Four sodium tetrafluoroborate directed supramolecular networks having 3- and 3,8-disubstituted 1,10-phenanthroline ligands



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ABSTRACT

Four novel sodium tetrafluoroborate directed supramolecular networks having 3- and 3,8-disubstituted 1,10-phenanthroline (phen) ligands, formulated as $[\text{Na}(3\text{-bromo-phen})_2\text{BF}_4]$ (**1**), $[\text{Na}(3\text{-bromo-phen})\text{BF}_4]_4$ (**2**), $[\text{Na}(3,8\text{-dibromo-phen})\text{BF}_4]_n$ (**3**) and $[\text{Na}(3\text{-(thiophen-2'-yl)-phen})\text{BF}_4]_n$ (**4**), have been prepared and structurally characterized, together with 3,8-dibromo-1,10-phenanthroline (**5**). Versatile coordination numbers for the sodium(I) centers (varying from 3, 4, 6 to 7) and coordination modes for the phen-based ligands (monodentate and bidentate) have been observed, where different coordinating and bridging fashions for the tetrafluoroborate anions as well as dissimilar intermolecular π - π stacking and hydrogen bonding interactions have been found in mononuclear complex **1**, tetranuclear complex **2**, one-dimensional (1D) and two-dimensional (2D) coordination polymers **3** and **4**. By checking the latest version of CCDC databases, it is found that the structural examples are all very rare on the monodentate coordination mode for the phen-based ligand, the presence of three and four-coordinate sodium(I) coordination centers and the sodium(I)-thiophene coordination bonds.

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1. Introduction

Coordination polymers have been extensively investigated in recent decades, producing various architectures that are rationally constructed from a variety of molecular building blocks and interactions between them [1–3]. Compared with the supramolecular frameworks based upon transition-metal ions, sodium(I) ion mediated self-assemblies are less involved because of its weak coordination ability [4–6]. On the other hand, tetrafluoroborate anion is commonly used as a counterion, which is not involved in the formation of coordinative bond with transition-metal ions also because of its weak coordination ability [7–10].

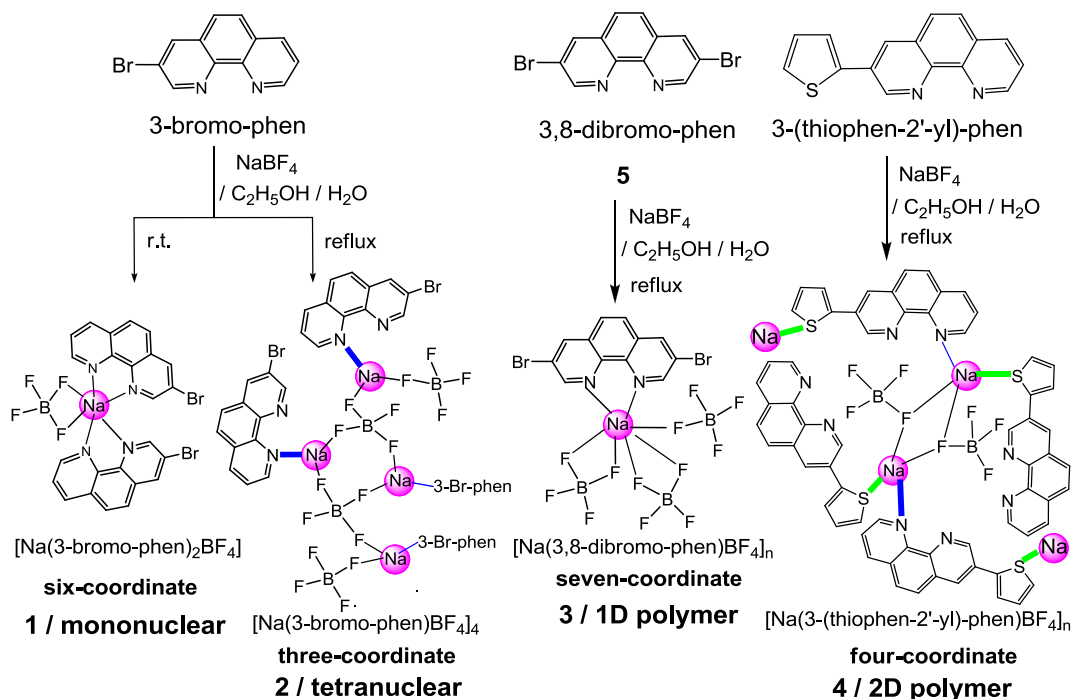
However, from the viewpoint of Hard–Soft–Acid–Base theory, fluorine is a hard element and in some cases it can be coordinated with a hard acid like a sodium(I) ion. Actually, sodium(I) tetrafluoroborate is often used as a salt to help precipitate the metal complexes by its large anionic effect, but studies on the sodium(I) tetrafluoroborate sustained supramolecular networks and coordination polymers having certain organic building blocks are not well performed, mainly because of the weak coordination ability of sodium(I) cation and tetrafluoroborate anion as well as the difficulties in obtaining their single-crystal structures [11–15]. In our

previous study, we have used the sodium(I) ion as a template to synthesize some macrocyclic complexes [16], which can also be regarded as a kind of self-assembly to some extent. In addition, some sodium(I) ion directed three-dimensional self-assemblies with some pyridinecarboxylates (3,5-pyridinedicarboxylate and 4-pyridinecarboxylate) [17] as well as certain chiral molecules such as (1R,3S)-1-monoamidocamphoric acid [18] have been reported. In particular, we have described a novel single-strand helical coordination polymer directed by sodium(I) tetrafluoroborate and 1,10-phenanthroline (phen) in which the BF_4^- anion acts as a new μ_3 bridging ligand [19].

To make systematic investigations on this issue, we have extended our work and reported herein four new sodium tetrafluoroborate directed supramolecular networks **1–4** having 3-bromo, 3,8-dibromo and 3-(thiophen-2'-yl)-phen ligands (Scheme 1), in which diverse coordination fashions have been observed for the central sodium(I) ion (varying from tridentate to septdentate) and the phen-based ligands (monodentate and bidentate). Moreover, the tetrafluoroborate anions exhibit different bridging modes with the sodium(I) ions in **1–4**. They are mononuclear complex **1** $[\text{Na}(3\text{-bromo-phen})_2(\text{BF}_4)]$ with one six-coordinate sodium(I) center, tetranuclear complex **2** $[\text{Na}(3\text{-bromo-phen})\text{BF}_4]_4$ with four three-coordinate sodium(I) centers, 1D coordination polymer **3** $[\text{Na}(3,8\text{-dibromo-phen})\text{BF}_4]_n$ with seven-coordinate sodium(I) centers, and 2D coordination polymer **4** $[\text{Na}(3\text{-(thiophen-2'-yl)-phen})\text{BF}_4]_n$ with four-coordinate sodium(I) centers and uncommon

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Scheme 1. Schematic illustration for the preparation of sodium(I) complexes **1–4** with different nuclearities and coordination modes for the central sodium(I) ions. The unusual monodentate coordination fashion for the phen-based ligands in **2** and **4** as well as the sodium(I)–thiophene coordination bonds in **4** are shown in blue and green color, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

sodium(I)–thiophene coordination bonds. In addition, the single-crystal structure of 3,8-dibromo-phen (**5**) has been included showing a 1D double ribbon structure linked by the $\text{Br} \cdots \text{Br}$ contacts.

2. Experimental

2.1. Materials and physical measurements

All reagents and solvents were of analytical grade and used without further purification. UV–Vis spectra were recorded with a Shimadzu UV-3150 double-beam spectrophotometer using a quartz cell with a path length of 10 mm at room temperature. Infrared spectra (IR, 4000–400 cm^{-1}) were determined in a Horiba FT-700 spectrophotometer. Analyses for carbon, hydrogen and nitrogen were performed on a Perkin-Elmer 1400C analyzer. ^1H NMR spectra were collected on a Varian Unit 500 MHz spectrometer and a JEOL GSX 270 MHz spectrometer. Electrospray ionization mass spectra (ESI-MS) were recorded on a Finnigan MAT S500 mass spectrometer in a scan range 100–1200 amu.

2.2. Syntheses of $[\text{Na}(\text{3-bromo-phen})_2\text{BF}_4]$ (**1**) and $[\text{Na}(\text{3-bromo-phen})\text{BF}_4]_4$ (**2**)

A mixture of sodium tetrafluoroborate (0.055 g, 0.5 mmol) in 10 cm^3 water and 3-bromo-phen (0.259 g, 1.0 mmol) in 40 cm^3 ethanol was stirred at room temperature for 2 h. The mixture was concentrated to nearly dry using a rotatory evaporator, and then the resulting precipitate **1** was filtered and washed by diethyl ether and dried in a vacuum. Yield: 0.22 g (70.1%). Main IR (KBr pellets, cm^{-1}): 3052 (w), 1617 (m), 1577 (m), 1560 (m), 1499 (m), 1420 (s), 1099 (vs), 1080 (vs), 1056 (vs), 900 (s), 873 (m), 839 (m), and 731 (s). Elemental *Anal.* Calc. for $\text{NaC}_{12}\text{H}_7\text{Br}_2\text{N}_4\text{BF}_4$: C, 45.90; H, 2.25; N, 8.92. Found: C, 45.96; H, 2.39; N, 8.99%. ^1H NMR (500 MHz, CD_3COCD_3 , ppm): 9.12 (dd, 2H, $J = 1.70$ and 1.70 Hz, H9), 9.10 (d, 2H, $J = 2.20$ Hz, H2), 8.76 (d, 2H, $J = 2.45$ Hz, H4), 8.53 (dd, 2H, $J = 1.70$ and 1.70 Hz, H7), 8.08 (d, 2H,

$J = 9.05$ Hz, H5), 7.99 (d, 2H, $J = 9.05$ Hz, H6), 7.82 (dd, 2H, $J = 4.35$ and 4.15 Hz, H8). ESI-MS: m/z 541 $[\text{Na}(\text{3-bromo-1,10-phenanthroline})_2]^+$, 100%. UV–Vis in water: $\lambda_{\text{max}} = 235, 271$ and 293 nm.

A mixture of stoichiometric amounts of sodium tetrafluoroborate (0.110 g, 1.0 mmol) in 10 cm^3 water and 3-bromo-phen (0.259 g, 1.0 mmol) in 40 cm^3 ethanol was refluxed for 2 h. The mixture was cooled to room temperature and concentrated to nearly dry using a rotatory evaporator, and then the resulting precipitate **2** was filtered and washed by diethyl ether and dried in a vacuum. Yield: 0.28 g (75.9%). Main IR (KBr pellets, cm^{-1}): 3018 (m), 1618 (s), 1588 (s), 1576 (s), 1542 (s), 1466 (s), 1387 (m), 1338 (m), 1308 (s), 1088 (vs), 1067 (vs), 1051 (vs), 903 (s), 839 (m), 713 (s), and 522 (m). Elemental *Anal.* Calc. for $\text{NaC}_{12}\text{H}_7\text{Br}_2\text{N}_2\text{BF}_4$: C, 39.07; H, 1.91; N, 7.59. Found: C, 39.20; H, 2.01; N, 7.55%. ^1H NMR (500 MHz, CD_3COCD_3 , ppm): 9.61 (dd, 1H, $J = 6.80$ and 5.85 Hz, H9), 9.53 (dd, 1H, $J = 7.10$ and 5.60 Hz, H2), 9.34 (d, 1H, $J = 4.90$ Hz, H4), 9.09 (d, 1H, $J = 1.95$ Hz, H7), 8.59 (d, 1H, $J = 8.30$ Hz, H5), 8.50 (d, 1H, $J = 9.05$ Hz, H6), 8.42 (dd, 1H, $J = 2.70$ and 2.70 Hz, H8). ESI-MS: m/z 282 $[\text{Na}(\text{3-bromo-phen})]^+$, 100%. UV–Vis in water: $\lambda_{\text{max}} = 233, 272$ and 311 nm. Colorless needlelike single crystals of **1** and **2** suitable for X-ray diffraction determination were grown from a mixed solution of acetone and water ($v/v = 3:1$) by slow evaporation in air at room temperature.

2.3. Syntheses of $[\text{Na}(\text{3,8-dibromo-phen})\text{BF}_4]_n$ (**3**) and $[\text{Na}(\text{3-(thiophen-2'-yl)-phen})\text{BF}_4]_n$ (**4**)

1D and 2D coordination polymers **3** and **4** were synthesized via the similar method as that of **2** except that 3,8-dibromo-phen (0.338 g, 1.0 mmol) in the case of **3** and 3-(thiophen-2'-yl)-phen (0.262 g, 1.0 mmol) in the case of **4** were used, respectively. **3**: Yield: 0.35 g (78.1%). Main IR (KBr pellets, cm^{-1}): 1653 (m), 1636 (m), 1617 (s), 1560 (m), 1306 (m), 1098–1040 (vs), 772 (s), 723 (m), and 622 (s). Elemental *Anal.* Calc. for $\text{NaC}_{12}\text{H}_6\text{Br}_2\text{N}_2\text{BF}_4$: C, 32.19; H, 1.35; N, 6.26. Found: C, 32.35; H, 1.49; N, 6.42%. ^1H NMR (500 MHz, CD_3COCD_3 , ppm): 9.31 (d, 2H, $J = 2.20$ Hz, H2 and H9), 9.02 (d, 2H, $J = 2.20$ Hz, H4 and H7), 8.20 (s, 2H, H5 and H6).

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