

Supramolecular Incarceration and Extraction of Tetrafluoroberyllate from Water by Nanojars

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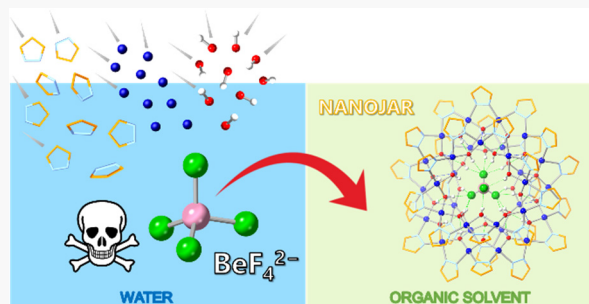
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ABSTRACT: The previously unexplored noncovalent binding of the highly toxic tetrafluoroberyllate anion (BeF_4^{2-}) and its extraction from water into organic solvents are presented. Nanojars resemble anion-binding proteins in that they also possess an inner anion binding pocket lined by a multitude of H-bond donors (OH groups), which wrap around the incarcerated anion and completely isolate it from the surrounding medium. The BeF_4^{2-} -binding propensity of $[\text{BeF}_4\text{C}\{\text{Cu}^{\text{II}}(\text{OH})(\text{pz})\}_n]^{2-}$ (pz = pyrazolate; n = 27–32) nanojars of different sizes is investigated using an array of techniques including mass spectrometry, paramagnetic ^1H , ^9Be , and ^{19}F NMR spectroscopy, and X-ray crystallography, along with thermal stability studies in solution and chemical stability studies toward acidity and Ba^{2+} ions.

The latter is found to be unable to precipitate the insoluble BaBeF_4 from nanojar solutions, indicating a very strong binding of the BeF_4^{2-} anion by nanojars. ^9Be and ^{19}F NMR spectroscopy allows for the unprecedented direct probing of the incarcerated anion in a nanojar and, along with ^1H NMR studies, reveals the fluxional structure of nanojars and their inner anion-binding pockets. Single-crystal X-ray diffraction provides the crystal and molecular structures of $(\text{Bu}_4\text{N})_2[\text{BeF}_4\text{C}\{\text{Cu}(\text{OH})(\text{pz})\}_{32}]$, which contains a novel Cu_x -ring combination (x = 9 + 14 + 9), $(\text{Bu}_4\text{N})_2[\text{BeF}_4\text{C}\{\text{Cu}(\text{OH})(\text{pz})\}_{8+14+9}]$, and $(\text{Bu}_4\text{N})_2[\text{BeF}_4\text{C}\{\text{Cu}(\text{OH})(\text{pz})\}_{6+12+10}]$ and offers detailed structural parameters related to the supramolecular binding of BeF_4^{2-} in these nanojars. The extraction of BeF_4^{2-} from water into organic solvents, including the highly hydrophobic solvent *n*-heptane, demonstrates that nanojars are efficient binding and extracting agents not only for oxoanions but also for fluoroanions.



1. INTRODUCTION

Beryllium (Be) is one of the most toxic and carcinogenic nonradioactive elements.^{1,2} If inhaled, it can cause acute Be poisoning, chronic Be disease (berylliosis), and lung cancer, which are incurable and can be fatal.³ However, Be is highly desirable for various applications because of a unique combination of physicochemical properties.⁴ Its low density (over 30% lighter than aluminum), high melting point (almost double that of aluminum), exceptional flexural rigidity (a Young's modulus that is 4 times greater than that of aircraft aluminum alloy), and resistance to corrosion make Be and Be–Al alloys outstanding structural materials for the aerospace industry. Be–Cu alloys with ~2% Be are 6 times stronger than pure Cu and are extensively used in critical moving parts of aircraft engines, as key components of precision instruments, and as nonsparking tools used in high-explosion-risk environments. Be is also used in nuclear and radiation technology. BeO is a refractory and ideal heat-sink material for electronics, being an excellent electrical insulator with high thermal conductivity. From processors for quantum computers⁵ to mirrors for the recently launched James Webb Space Telescope,⁶ Be and its alloys/compounds continue to find a growing number of applications in diverse fields.⁷

The presence of fluoride exacerbates the toxicity of aqueous Be⁸ because of formation of the tetrafluoroberyllate ion (BeF_4^{2-}), which mimics the γ -phosphate group of guanosine triphosphate and interferes with the GTPase activity of G proteins.⁹ As opposed to the $\text{Be}(\text{H}_2\text{O})_4^{2+}$ ion, BeF_4^{2-} is stable against hydrolysis and precipitation from water.¹⁰ Tetrafluoroberyllates are encountered in various technologies, such as coolants and solvents in nuclear reactors,¹¹ intermediates in the production of Be metal,¹² and precursors for deep-UV nonlinear-optical materials.¹³ Although several supramolecular receptors for the binding, transport, and extraction of a variety of small inorganic anions from water have been developed,^{14–22} the supramolecular binding of BeF_4^{2-} has hitherto been uncharted. In fact, only nine structurally characterized compounds that contain a discrete BeF_4^{2-} ion (as a counterion for protonated amines²³ and mononuclear Cu^{2+} and Co^{3+}

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coordination complexes)²⁴ are found in the Cambridge Structural Database.

Nanojars, supramolecular coordination complexes of the formula $[\text{anionC}\{\text{cis-Cu}^{\text{II}}(\mu\text{-OH})(\mu\text{-pz})\}_n]^{2-}$ [Cu_n ; $n = 26\text{--}36$; pz = pyrazolate ($\text{C}_3\text{H}_3\text{N}_2^-$)],²⁵ have been successfully used for the binding of oxoanions with large hydration energy such as CO_3^{2-} ,^{26–31} SO_4^{2-} ,^{32–34} SeO_3^{2-} ,³⁵ HPO_3^{2-} ,³⁵ HPO_4^{2-} ,³⁶ and HAsO_4^{2-} .³⁶ Herein, we demonstrate that nanojars are excellent supramolecular binding agents not only for oxoanions but also for the fluoroanion BeF_4^{2-} , which was extracted from water and transferred into organic solvents (including aliphatic hydrocarbons) by liquid–liquid extraction. The BeF_4 -incarcerating nanojars presented here are the first supramolecular assemblies in which BeF_4^{2-} is noncovalently bound, exclusively by H-bonding. Electrospray ionization mass spectrometry (ESI-MS), variable-temperature (VT), paramagnetic ^1H , ^9Be , and ^{19}F NMR spectroscopy, X-ray crystallography, and competitive anion-binding studies offer details about the intricacies of BeF_4^{2-} binding by nanojars. ^9Be and ^{19}F NMR spectroscopy allows for the direct probing of the incarcerated anion inside the nanojar for the first time. Furthermore, single-crystal X-ray diffraction is employed to characterize three different BeF_4 -incarcerating nanojars.

2. RESULTS AND DISCUSSION

Synthesis and Characterization by Mass Spectrometry. A mixture of BeF_4 -incarcerating nanojars of the formula $(\text{Bu}_4\text{N})_2[\text{BeF}_4\text{C}\{\text{cis-Cu}^{\text{II}}(\mu\text{-OH})(\mu\text{-pz})\}_n]$ (Cu_nBeF_4 ; $n = 27\text{--}32$) was obtained from the reaction of $\text{Cu}(\text{NO}_3)_2$ with pyrazole, $(\text{Bu}_4\text{N})_2\text{BeF}_4$, and Bu_4NOH (1:1:1:2 molar ratio) in tetrahydrofuran (THF). ESI-MS(–) analysis reveals the presence of nanojars with $n = 27$ (m/z 2035), 28 (m/z 2109), 29 (m/z 2183), and 31 (m/z 2331), as well as small amounts of nanojars with $n = 30$ (m/z 2257) and 32 (m/z 2404) (Figure 1A). On the basis of their different solubilities in toluene, the smaller $\text{Cu}_{27}\text{BeF}_4$ and $\text{Cu}_{28}\text{BeF}_4$ nanojars can be separated from the larger nanojars by selective crystallization. Thus, when a clear solution of Cu_nBeF_4 ($n = 27\text{--}32$) in toluene is left standing in a closed vessel for 48 h, a precipitate settles out, and it is identified by ESI-MS(–) as a mixture of $\text{Cu}_{27}\text{BeF}_4$ and $\text{Cu}_{28}\text{BeF}_4$ (Figure 1B). Conversely, the filtrate consists mostly of the larger $\text{Cu}_{29}\text{BeF}_4$ and $\text{Cu}_{31}\text{BeF}_4$ nanojars, with small amounts of nanojars of other sizes (Figure 1C).

When the nanojar synthesis is carried out by stirring $\text{CuBeF}_4\cdot\text{SH}_2\text{O}$, pyrazole, NaOH, and Bu_4NOH in THF in the presence of PbBeF_4 (29:29:56:2:13 molar ratio), $\text{Cu}_{31}\text{BeF}_4$ is obtained almost exclusively (with traces of $\text{Cu}_{32}\text{BeF}_4$; Figure 1D). This is attributable to the slight acidity provided by the $\text{Pb}^{2+}(\text{aq})$ ion ($\text{p}K_a = 7.6$),³⁷ which promotes the breakdown of more vulnerable, smaller nanojars and leads to the formation of $\text{Cu}_{31}\text{BeF}_4$, the most stable nanojar with BeF_4^{2-} . PbBeF_4 is poorly soluble in water (the solubility of the isomorphous PbSO_4 is 4.4 mg/100 mL of water at 25 °C; $K_{\text{sp}} = 2.53 \times 10^{-8}$),³⁸ which is crucial for preventing the complete breakdown of nanojars induced by acidity.²⁸

X-ray Crystallography. Single-crystal X-ray diffraction analysis of $(\text{Bu}_4\text{N})_2[\text{BeF}_4\text{C}\{\text{cis-Cu}^{\text{II}}(\mu\text{-OH})(\mu\text{-pz})\}_{9+14+9}]$ ($\text{Cu}_{32}\text{BeF}_4$; **1**), $(\text{Bu}_4\text{N})_2[\text{BeF}_4\text{C}\{\text{cis-Cu}^{\text{II}}(\mu\text{-OH})(\mu\text{-pz})\}_{8+14+9}]$ ($\text{Cu}_{31}\text{BeF}_4$; **2**), and $(\text{Bu}_4\text{N})_2[\text{BeF}_4\text{C}\{\text{cis-Cu}^{\text{II}}(\mu\text{-OH})(\mu\text{-pz})\}_{6+12+10}]$ ($\text{Cu}_{28}\text{BeF}_4$; **3**) offers detailed information about binding of the BeF_4^{2-} anion inside the nanojar cavity (Tables S1–S8 and Figures S4–S6). The structures of **2** and **3** are isomorphous with the corresponding $\text{Cu}_{31}\text{SO}_4$ and $\text{Cu}_{28}\text{SO}_4$

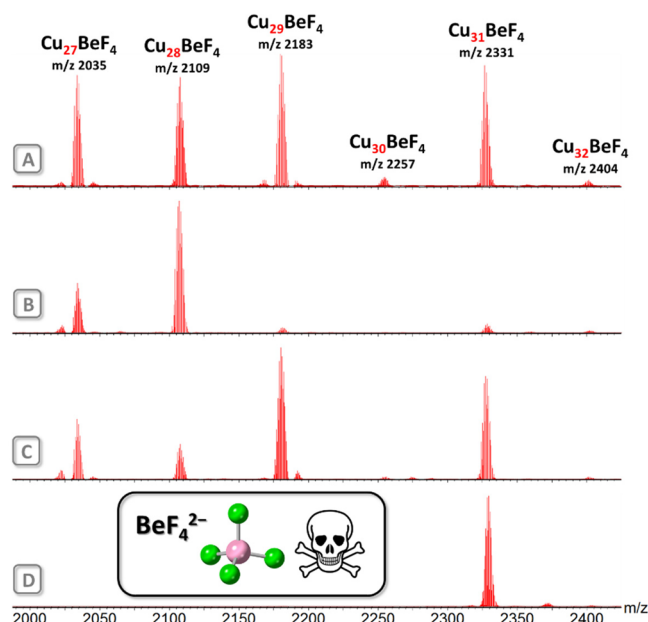


Figure 1. ESI-MS(–) spectra in CH_3CN of (A) the as-synthesized tetrafluoroberyllate-incarcerating nanojar mixture $[\text{BeF}_4\text{C}\{\text{Cu}(\text{OH})(\text{pz})\}_n]^{2-}$ (Cu_nBeF_4 ; $n = 27\text{--}32$), (B) the fraction crystallized out of a toluene solution, (C) the fraction soluble in toluene, and (D) $\text{Cu}_{31}\text{BeF}_4$ obtained with PbBeF_4 as an additive during synthesis. Detailed isotopic distributions are shown in Figure S1.

analogues,³² whereas the structure of **1** is novel because an analogous $\text{Cu}_{32}\text{SO}_4$ structure is not available.

In the noncentrosymmetric crystal lattice (orthorhombic, $P2_12_12_1$) of **1**, the nanojar units are located on general positions and pack in an unprecedented manner around 2_1 screw axes running along the c axis of the unit cell (Figure S7). The new Cu_{32} nanojar consists of three stacked $[\text{cis-Cu}^{\text{II}}(\mu\text{-OH})(\mu\text{-pz})]_x$ metallamacrocycles ($x = 9, 14, 9$) and has a distinct structure compared to other crystallographically characterized nanojars. In particular, the Cu_{14} central ring is saddle-shaped, whereas the two Cu_9 side rings are taco-shaped and are related to each other approximately by an S_4 improper rotation (Figure 2). The taco shape of the two Cu_9 side rings provides excellent binding pockets for the two Bu_4N^+ counterions, with two butyl arms of each Bu_4N^+ moiety nesting between the two flaps of each Cu_9 ring (Figure S8).

The primary coordination environment around the Cu centers is approximately square-planar, with deviations from the $\text{cis-O}_2\text{CuN}_2$ mean plane ranging from 0.04 to 0.23 Å (average of the largest deviations for each of the 32 Cu atoms: 0.12 Å). Although differently shaped, $\text{Cu}_{32}\text{BeF}_4$ (**1**) displays Cu–O and Cu–N bond lengths similar to those found in the $\text{Cu}_{31}\text{BeF}_4$ (**2**) and $\text{Cu}_{28}\text{BeF}_4$ (**3**) nanojars, with virtually identical averages of 1.932(4) and 1.976(5) Å, respectively (Table S2). The O atoms of the central Cu_{14} ring form seven axial $\text{Cu}\cdots\text{O}$ interactions with each of the two Cu_9 side rings [avg. 2.530(4) Å; only seven Cu atoms of each of the Cu_9 rings and none of the Cu_{14} rings have an axial O atom within the sum of the van der Waals radii of Cu and O of 2.92 Å], whereas the corresponding H atoms form alternating H bonds with OH groups of the two Cu_9 side rings [avg. O $\cdots$ O distance: 2.800(6) Å]. In turn, the OH groups of the two Cu_9 side rings form H bonds with the incarcerated BeF_4^{2-} anion [avg. O $\cdots$ F distance: 2.92(3) Å].

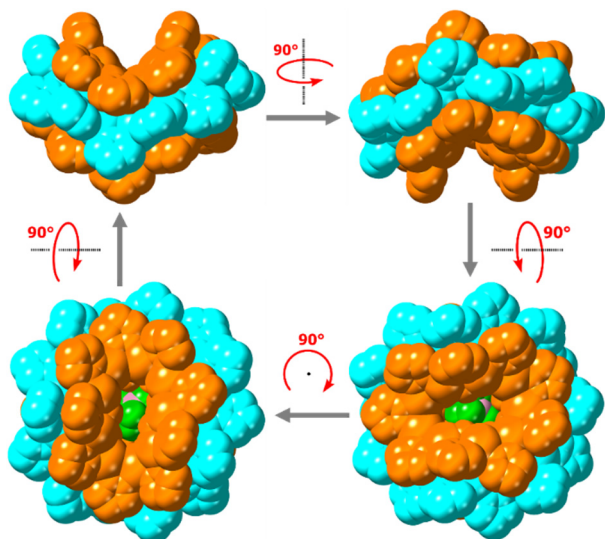


Figure 2. Space-filling representation of the crystal structure of **1** illustrating the saddle shape of the Cu_{14} ring and the taco shape of the Cu_9 ring. Color code: orange, Cu_9 ring; cyan, Cu_{14} ring.

In **1**–**3**, the central anion-binding pocket is lined by a multitude of OH groups, which offer various H-bonding sites for the BeF_4^{2-} anion. Thus, the latter is found to be disordered over three (in **1**, with an occupancy ratio of 0.60/0.19/0.21) or two (in **2** and **3**, with occupancy ratios of 0.68/0.32 and 0.69/0.31) positions, which differ from each other mainly in the location of the F atoms. Despite the virtually identical average H-bonded $\text{O}\cdots\text{F}$ distance of 2.92(3) Å in **1**–**3** (based on 12–15 H bonds with $\text{O}\cdots\text{F}$ distances shorter than 3.2 Å; Table S2), the binding of the BeF_4^{2-} anion in **1**–**3** is quite different

(Figure 3). As described in the NMR section below, heating of a Cu_nBeF_4 ($n = 27$ – 32) mixture in dimethyl sulfoxide (DMSO)- d_6 to 150 °C leads to the gradual conversion of nanojars of different sizes into $\text{Cu}_{31}\text{BeF}_4$, which appears to be the most stable one with BeF_4 . This observation is correlated with the structural differences observed. For example, $\text{Cu}_{28}\text{BeF}_4$ and $\text{Cu}_{31}\text{BeF}_4$ form in approximately equal amounts during the kinetically controlled synthesis of nanojars (Figure 1a). In $\text{Cu}_{28}\text{BeF}_4$, one F atom of the BeF_4^{2-} anion forms six H bonds with the bowl-shaped Cu_6 ring, whereas the other three F atoms form only two H bonds each with the relatively flat Cu_{10} ring. In $\text{Cu}_{31}\text{BeF}_4$, however, the Cu_8 and Cu_9 side rings are both puckered, orienting their H-bond donor OH groups deeper into the anion-binding cavity and providing a more optimal, closer to spherical H-bonding environment for the BeF_4^{2-} anion.

^1H NMR Spectroscopy. While ESI-MS displays four major peaks and provides only the size of the nanojars, NMR is able to distinguish between isomeric forms, such as Cu_{7+13+9} and Cu_{8+13+8} in the case of the $\text{Cu}_{29}\text{BeF}_4$ nanojar. Thus, the ^1H NMR spectrum of the Cu_nBeF_4 ($n = 27$ – 32) nanojar mixture in $\text{DMSO}-d_6$ displays five major overlapping sets of peaks corresponding to $\text{Cu}_{6+12+9}\text{BeF}_4$, $\text{Cu}_{6+12+10}\text{BeF}_4$, $\text{Cu}_{7+13+9}\text{BeF}_4$, $\text{Cu}_{8+13+8}\text{BeF}_4$, and $\text{Cu}_{8+14+9}\text{BeF}_4$, as well as minor peaks corresponding to $\text{Cu}_{30}\text{BeF}_4$ (Cu_{7+14+9} and Cu_{8+14+8}) and $\text{Cu}_{32}\text{BeF}_4$ ($\text{Cu}_{8+14+10}$ and Cu_{9+14+9}) (Figure 4 and Table S9). The presence of paramagnetic Cu^{2+} ions in nanojars leads to a drastic downfield shift of the peaks corresponding to pyrazolate protons (between 21 and 41 ppm at 25 °C) and an even more drastic upfield shift of the OH protons (between –26 and –61 ppm at 25 °C). The largest shifts are observed in the case of the Cu_{10} ring of the Cu_{28} nanojar, for both pyrazolate (40.25 ppm) and OH (–60.27 ppm) protons. Because analogous

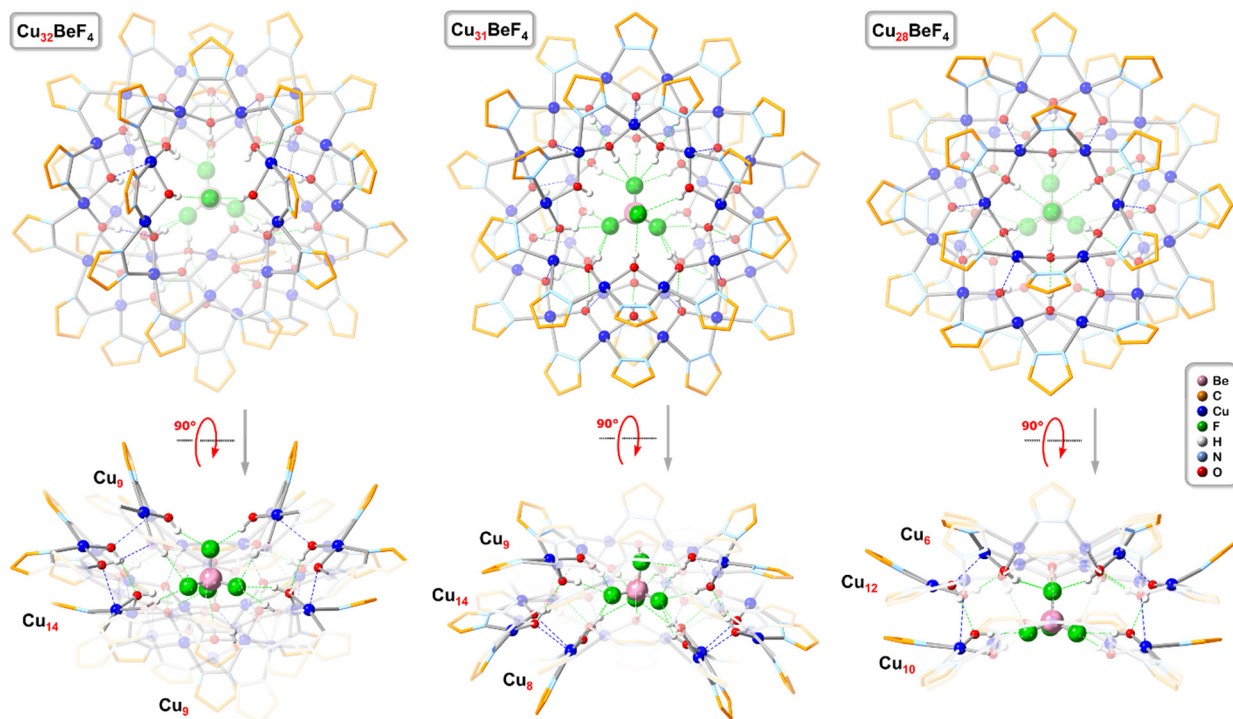


Figure 3. Ball-and-stick representation of the crystal structures of **1**–**3** (top and side views). Green and blue dotted lines indicate H bonds and axial $\text{Cu}\cdots\text{O}$ interactions, respectively. Counterions, lattice solvent molecules, and C–H bond H atoms are omitted for clarity, and only the major component is shown for disordered moieties.

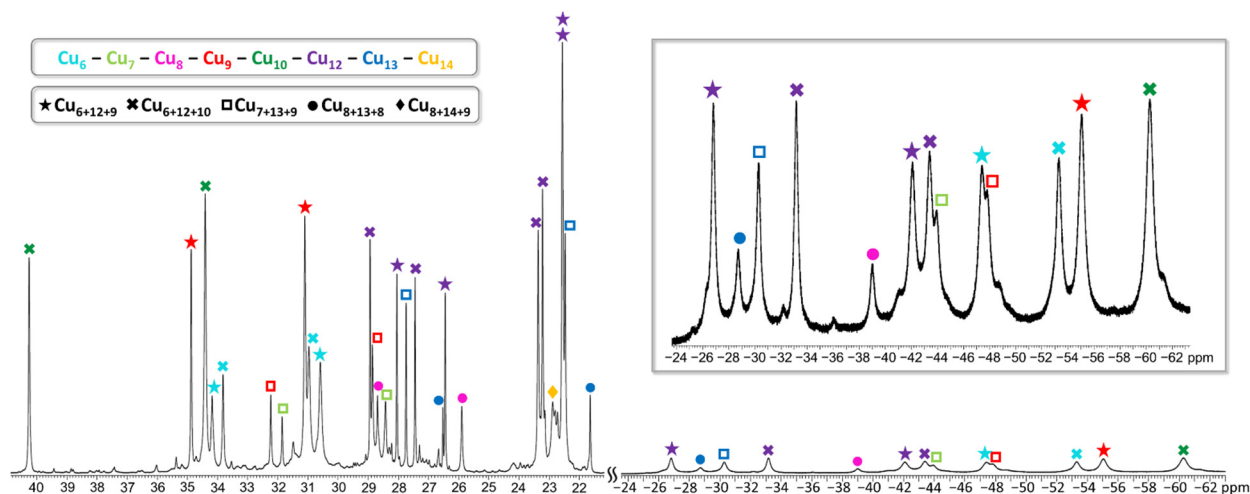


Figure 4. ^1H NMR spectrum (400 MHz, 25 $^\circ\text{C}$, $\text{DMSO}-d_6$) of the as-synthesized Cu_nBeF_4 ($n = 27\text{--}32$) nanojar mixture.

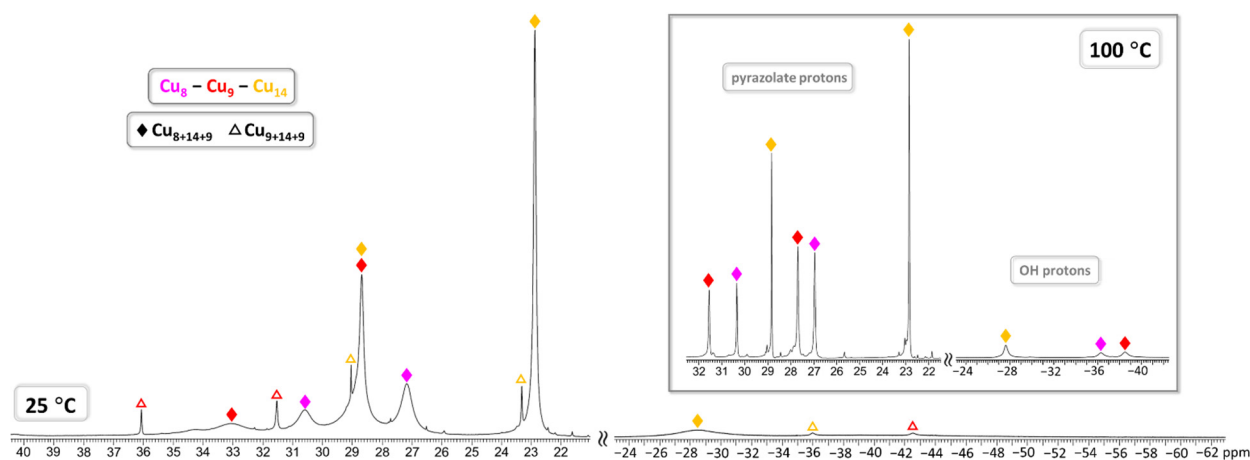


Figure 5. ^1H NMR spectrum (400 MHz, 25 $^\circ\text{C}$, $\text{DMSO}-d_6$) of the Cu_{8+14+9} nanojar (with small amounts of Cu_{9+14+9}).

nanojars with diamagnetic metal ions (such as Zn^{2+} or low-spin Fe^{2+}) cannot be obtained,³⁹ hyperfine shift values are not available.

The pyrazolate units have two magnetically distinct sets of protons: one for the 4 position and one for the 3 and 5 positions (with 1:2 integrated intensities). Within each Cu_x ring ($x = 6\text{--}14$, except 11), all pyrazolate and OH groups are magnetically identical, with the exception of the Cu_{12} ring, which shows two sets of signals of equal intensity for both the pyrazolate and OH protons in the $\text{Cu}_{6+12+9}\text{BeF}_4$ and $\text{Cu}_{6+12+10}\text{BeF}_4$ nanojars. In the latter nanojars, the two side rings (Cu_6 and Cu_9 or Cu_{10}) offer distinct magnetic environments so that the pyrazolate units of the central Cu_{12} ring, which are oriented toward either one or the other side ring in an alternating fashion, have markedly distinct chemical shifts for the protons in the 4 position (1.6 and 1.5 ppm differences for Cu_{27} and Cu_{28} , respectively). This magnetic inequivalence is less significant for the pyrazolate 3 and 5 positions (0.01 and 0.15 ppm differences for Cu_{27} and Cu_{28}), whereas the OH protons of the Cu_{12} rings are affected to an even larger degree (15 and 10 ppm differences for Cu_{27} and Cu_{28}) because of the alternating H bonds formed with either the Cu_6 or $\text{Cu}_9/\text{Cu}_{10}$ rings.

The assignment of the 48 major peaks in the ^1H NMR spectrum of the Cu_nBeF_4 nanojar mixture was facilitated by

isolation of the $\text{Cu}_{27}/\text{Cu}_{28}$ - and $\text{Cu}_{29}/\text{Cu}_{31}$ -enriched fractions (Figures S9 and S10 and Table S10), as well as the Cu_{31} nanojar with small amounts of Cu_{32} (Figure 5 and Table S11). Thus, 12 peaks corresponding to each of the Cu_{6+12+9} and $\text{Cu}_{6+12+10}$ nanojars, 9 peaks corresponding to each of the Cu_{7+13+9} and Cu_{8+14+9} nanojars, and 6 peaks corresponding to the Cu_{8+13+8} nanojar were identified (Tables S9–S11). Signals of the Cu_{32} nanojar are detectable in the spectrum of the Cu_{31} sample containing small amounts of Cu_{9+14+9} (Figure 5 and Table S11). Peaks of the Cu_{30} nanojar could not be assigned because of the very low abundance of this species.

The paramagnetism of the Cu^{2+} ions also affects the nuclear relaxation rates of the ^1H nuclei, which results in paramagnetic relaxation enhancement manifested as a broadening of the peaks in the NMR spectrum. Moreover, the paramagnetism induces residual dipolar couplings that reduce the magnitude of the J coupling between nuclei. As a result, the splitting of the peaks is not detectable. The relatively sharp peaks observed suggest strong antiferromagnetic coupling between the Cu^{2+} centers of the Cu_x rings [average $\text{Cu}\cdots\text{Cu}$: 3.278(1) Å (Cu_{9+14+9}), 3.287(1) Å (Cu_{8+14+9}), 3.286(1) Å ($\text{Cu}_{6+12+10}$); average $\text{Cu}-\text{O}-\text{Cu}$: 116.2(2) $^\circ$ (Cu_{9+14+9}), 117.1(2) $^\circ$ (Cu_{8+14+9}), 116.7(1) $^\circ$ ($\text{Cu}_{6+12+10}$); also see Table S2]. Both pyrazolate and O(H) ligands have been documented to mediate such a coupling.⁴⁰ The most prominent broadening is

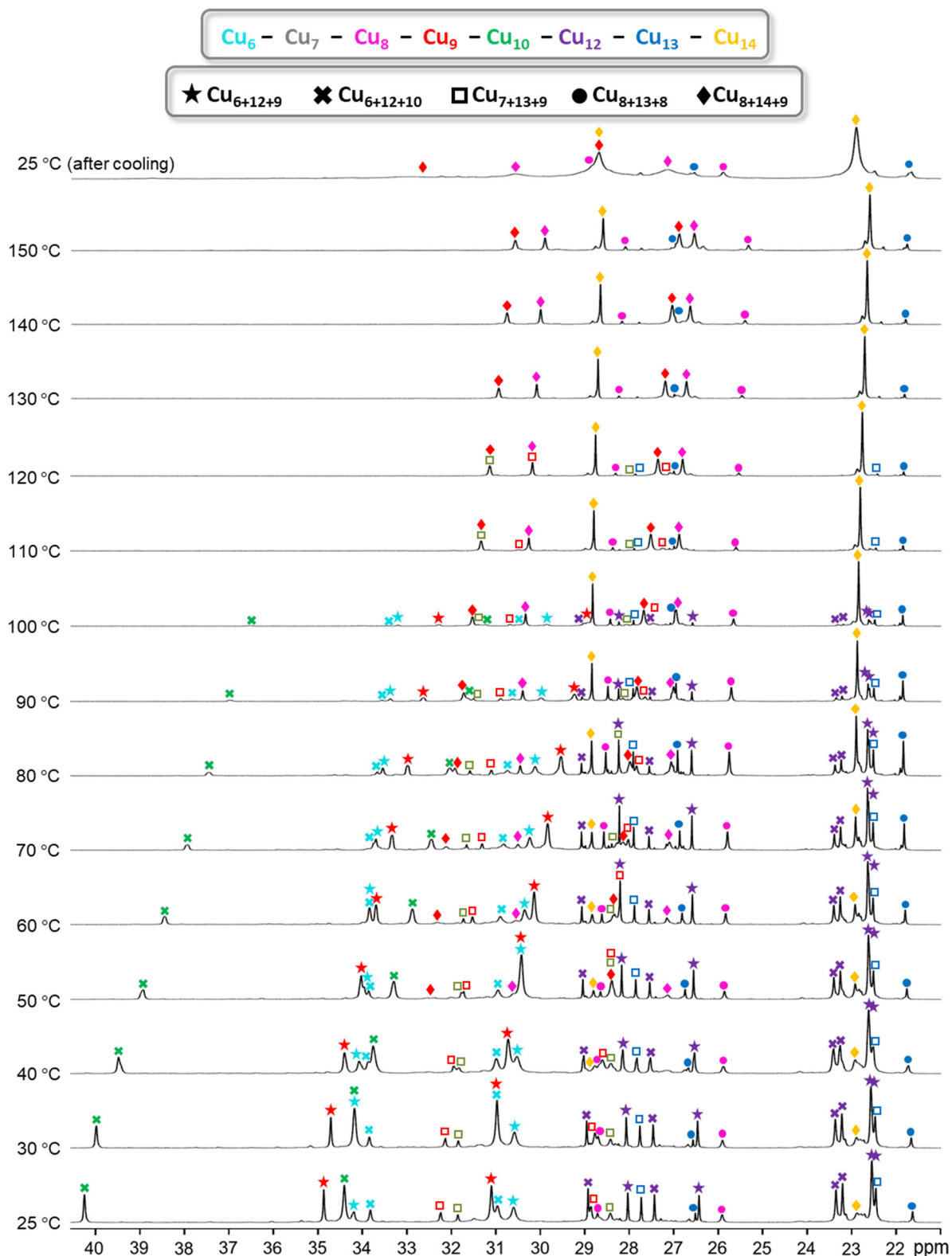


Figure 6. VT ^1H NMR spectra of the Cu_nBeF_4 ($n = 27\text{--}32$) nanojar mixture in $\text{DMSO-}d_6$, showing pyrazolate proton signals in the 21–41 ppm window. The given temperatures are the target temperatures of the probe.

observed in the case of the Cu_9 ring of the Cu_{8+14+9} nanojar, where the peaks are barely noticeable at room temperature (Figure 5). At higher temperatures, however, the peaks become significantly sharper. Moreover, the overlapping peaks of the 3/5 position of the Cu_9 ring and the 4 position

of the Cu_{12} ring resolve above 40 °C because of the different temperature dependences of their chemical shifts (Figures S11 and S12).

VT ^1H NMR measurements in $\text{DMSO-}d_6$ over the 25–150 °C range provide the varying degrees of temperature

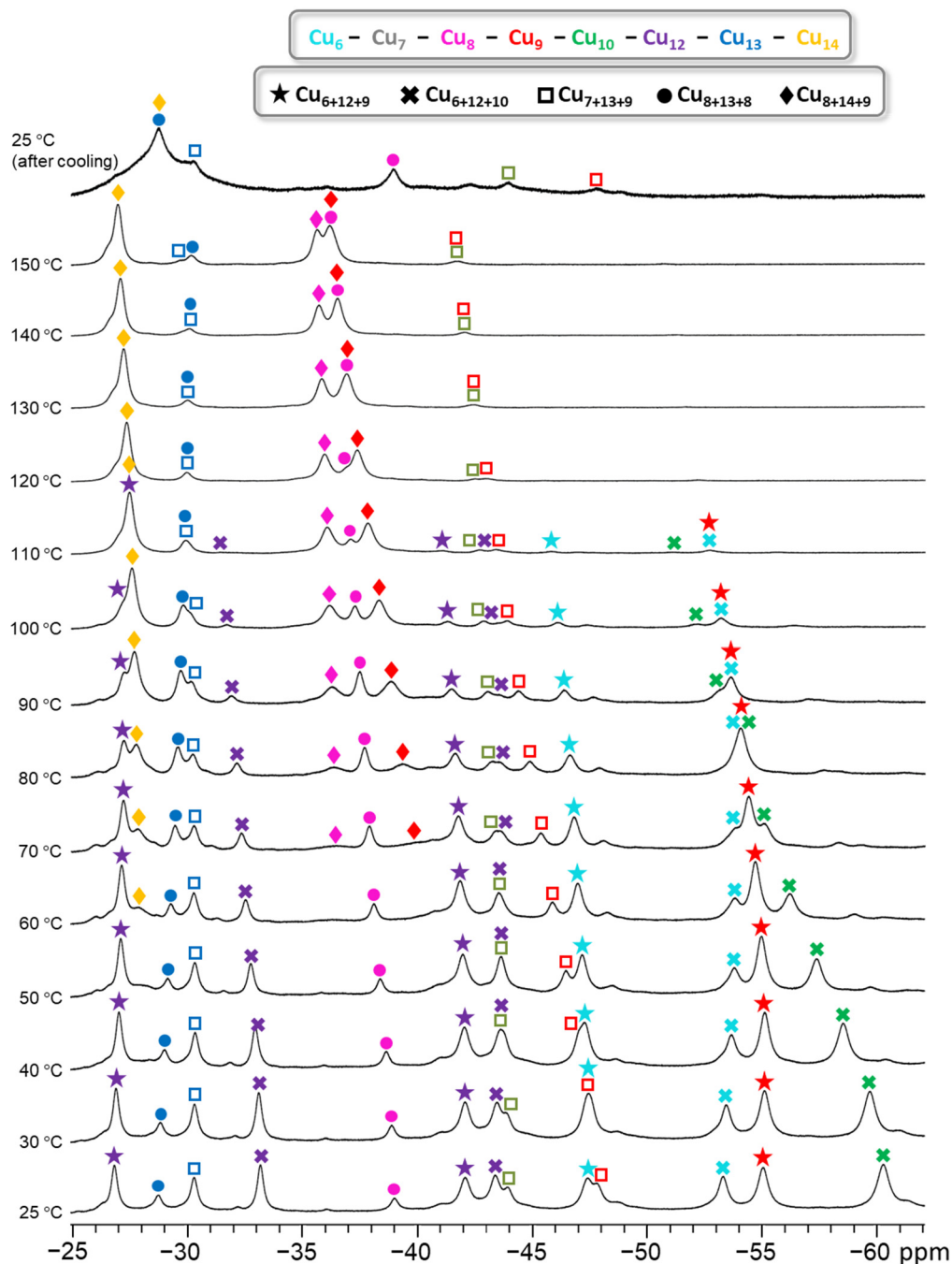


Figure 7. VT ^1H NMR spectra of the Cu_nBeF_4 ($n = 27\text{--}32$) nanojar mixture in $\text{DMSO-}d_6$, showing OH proton signals in the -25 to -62 ppm window. The given temperatures are the target temperatures of the probe.

dependence of the chemical shifts of different protons in BeF_4 nanojars (Tables S9–S11). The largest temperature-induced chemical shift change upon going from 25 to 120 $^\circ\text{C}$ is observed in the case of the Cu_{10} ring of the Cu_{28} nanojar, among both pyrazolate (a 4.7 ppm change for pz-4-H and a 4.0 ppm change for pz-3/5-H) and OH (a 10.0 ppm change) protons. The Cu_9 ring of the Cu_{27} , Cu_{29} , Cu_{31} , and Cu_{32} nanojars also displays large changes (a 1.9–3.3 ppm change for pz-4-H, a 1.4–2.9 ppm change for pz-3/5-H, and a 2.7–5.0 ppm change for OH), whereas the $\text{Cu}_6\text{--Cu}_8$ rings show smaller changes (a 0.4–1.4 ppm change for pyrazolate protons, and a 1.0–2.0 ppm change for OH protons). The corresponding change is negligible (a <0.2 ppm change for

pyrazolate protons) or very small (a 0.4–1.8 ppm change for OH protons) in the case of the larger, central $\text{Cu}_{12}\text{--Cu}_{14}$ rings. Curie plots of the ^1H NMR data (Figure S13), obtained by plotting the chemical shift (δ) as a function of $1/T$ over the temperature range from 25 to 120 $^\circ\text{C}$, show that all signals exhibit Curie-type behavior.

The VT ^1H NMR measurements also provide information about the thermal stability of nanojars of different sizes (Figures 6 and 7). Thus, a gradual transformation of Cu_{6+12+9} , $\text{Cu}_{6+12+10}$, and Cu_{7+13+9} into Cu_{8+13+8} and Cu_{8+14+9} nanojars is observed at increasing temperatures. Above 100 $^\circ\text{C}$, the peaks of the former three nanojars disappear from the ^1H NMR spectrum, and at 150 $^\circ\text{C}$, the Cu_{8+14+9} nanojar dominates.

Upon cooling, the spectrum shows mostly the presence of Cu_{8+14+9} and small amounts of Cu_{8+13+8} . Visual inspection of the NMR tube after the VT experiment shows no change in the appearance of the solution and the absence of any solid deposit, confirming the stability of the Cu_{8+14+9} nanojar (and to a smaller extent the Cu_{8+13+8} nanojar) at 150 °C in $\text{DMSO-}d_6$.

^9Be and ^{19}F NMR Spectroscopy. Owing to the NMR-active ^9Be (spin $3/2$) and ^{19}F (spin $1/2$) nuclei of the BeF_4^{2-} ion (both with a 100% natural abundance), the incarcerated anion inside the nanojar was directly probed for the first time. The ^9Be NMR signal of the free BeF_4^{2-} ion in $\text{DMSO-}d_6$ [as $(\text{Bu}_4\text{N})_2\text{BeF}_4$, referenced to a 0.43 M BeSO_4 solution in water in a coaxial NMR tube] appears at -0.54 ppm as a singlet. The observation of a singlet instead of the expected quintet (which is the case for Na_2BeF_4 in D_2O , with $J_{\text{Be-F}} = 34$ Hz; Figure S14) could be attributed to the higher viscosity of DMSO (2.24 cP) compared to water (1.00 cP). Upon incarceration in the Cu_{8+14+9} nanojar, the ^9Be chemical shift of the BeF_4^{2-} ion moves upfield by almost 13 units to -13.4 ppm (Figure 8). In

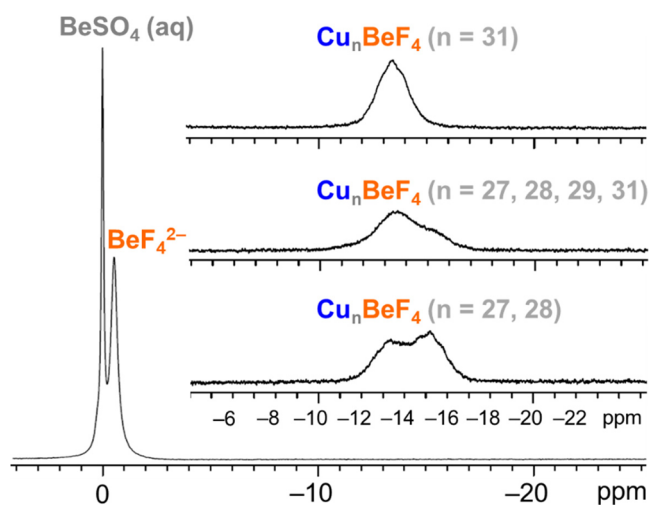


Figure 8. ^9Be NMR spectra (56 MHz, 25 °C, $\text{DMSO-}d_6$) of $(\text{Bu}_4\text{N})_2\text{BeF}_4$, the as-synthesized Cu_nBeF_4 ($n = 27\text{--}32$) nanojar mixture, the $\text{Cu}_{27}\text{BeF}_4/\text{Cu}_{28}\text{BeF}_4$ fraction, and $\text{Cu}_{31}\text{BeF}_4$.

the Cu_{6+12+9} and $\text{Cu}_{6+12+10}$ nanojars (as observed in the $\text{Cu}_{27}/\text{Cu}_{28}$ fraction), the corresponding signals are centered at -13.3 and -15.2 ppm, respectively, whereas the Cu_nBeF_4 nanojar mixture (consisting mostly of the Cu_{27} , Cu_{28} , Cu_{29} , and Cu_{31} nanojars) shows overlapping peaks of the four species. The upfield shift of the ^9Be signals as well as their broadening is due to the paramagnetic environment provided by the Cu^{2+} ions. Although the Be atom is approximately at the same distance from the Cu^{2+} centers (shortest $\text{Be}\cdots\text{Cu}$ distance: 4.9 Å) as the H atom at the pyrazolate 4 position (5.0 Å average), the chemical shifts of the ^9Be signals are less affected by the paramagnetic Cu^{2+} ions [a change of 13–15 ppm units, still within the -27.7 to $+44$ ppm window of known diamagnetic Be compounds⁴¹] than the ^1H signals (a change of 20–34 ppm units, compared to free pyrazole). This might reflect a better spin delocalization through bonds (four bonds from Cu to pz-4-H) versus through space. Nevertheless, the ^1H signals of the pyrazolate 3/5 positions, which are closer to the Cu^{2+} centers (3.3 Å average) and only three bonds away, are less affected (a change of 14–27 ppm units) than the pz-4-H protons.

The ^{19}F NMR signal of the free BeF_4^{2-} ion in $\text{DMSO-}d_6$ [$(\text{Bu}_4\text{N})_2\text{BeF}_4$, referenced to α,α,α -trifluorotoluene, $\text{CF}_3\text{C}_6\text{H}_5$, as an internal standard] is observed at -95.61 ppm as a singlet. Again, the loss of splitting (a quartet with $J_{\text{Be-F}} = 34$ Hz is observed in the case of Na_2BeF_4 in D_2O ; Figure S14) could be related to the higher viscosity of DMSO . As opposed to the ^9Be signals, which all move upfield upon incarceration of the BeF_4^{2-} ion in the various Cu_n nanojars, only the ^{19}F chemical shift corresponding to the Cu_{28} nanojar moves upfield by ~ 9 units to -104.97 ppm (Figure 9). The signals of the other

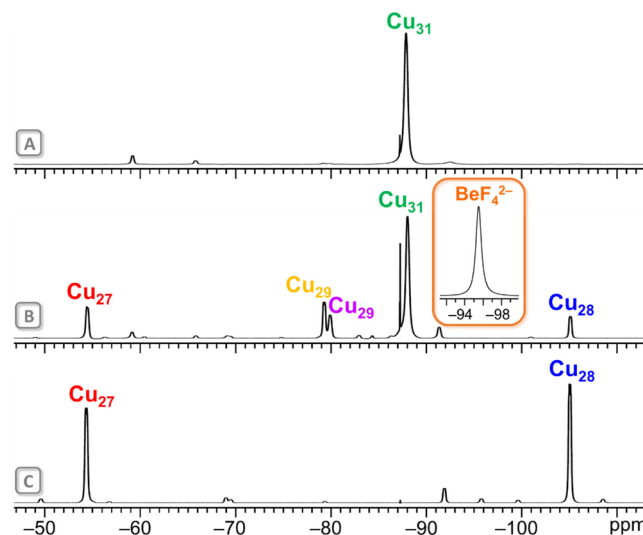


Figure 9. ^{19}F NMR spectra (376 MHz, 25 °C, $\text{DMSO-}d_6$) of $(\text{Bu}_4\text{N})_2\text{BeF}_4$ (inset), $\text{Cu}_{31}\text{BeF}_4$ (A), the as-synthesized Cu_nBeF_4 ($n = 27\text{--}32$) nanojar mixture (B), and the $\text{Cu}_{27}\text{BeF}_4/\text{Cu}_{28}\text{BeF}_4$ fraction (C).

nanojars shift downfield by ~ 8 units to -87.86 ppm (Cu_{31}), ~ 16 units to -79.89 ppm (Cu_{8+13+8}) and -79.26 ppm (Cu_{7+13+9}), and ~ 41 units to -54.32 ppm (Cu_{27}). Similar to the VT ^1H NMR experiments, VT ^{19}F NMR spectra indicate a substantial temperature dependence of the ^{19}F chemical shifts (Figure 10), manifested as changes of 3.0–7.7 ppm over the 25–100 °C range (Table S12). The observations are also in line with the VT ^1H NMR results, confirming the gradual transformation of the $\text{Cu}_{27}\text{--Cu}_{29}$ species into the most stable Cu_{31} nanojar at increasing temperatures. In addition, the spectra indicate that while at room temperature only the Cu_{7+13+9} species is present in this particular Cu_nBeF_4 sample, the other Cu_{29} species (Cu_{8+13+8}) forms upon heating.

Competitive BeF_4^{2-} Binding Studies. Because a guest-free nanojar host cannot be obtained and determination of an association constant by host–guest titration is precluded, the binding strength of BeF_4^{2-} by nanojars was assessed by competitive binding experiments using Ba^{2+} . Similar to BaSO_4 ($K_{\text{sp}} = 1.08 \times 10^{-10}$), the isomorphous BaBeF_4 is very poorly soluble in water⁴² and has been used for the gravimetric determination of Be.⁴³ After vigorously stirring a solution of Cu_nBeF_4 ($n = 27\text{--}29, 31$) in water-immiscible 2-methyltetrahydrofuran (2-MeTHF; Figure S2a) with an aqueous solution of $\text{Ba}(\text{NO}_3)_2$, followed by separation of the two layers, analysis of the organic phase by ESI-MS shows mostly the presence of the $\text{Cu}_{31}\text{BeF}_4$ nanojar (Figure S2b). The lack of the $\text{Cu}_{27}\text{--Cu}_{30}$ species points to a weaker binding of BeF_4^{2-} by these smaller nanojars. Nevertheless, the absence of nanojar

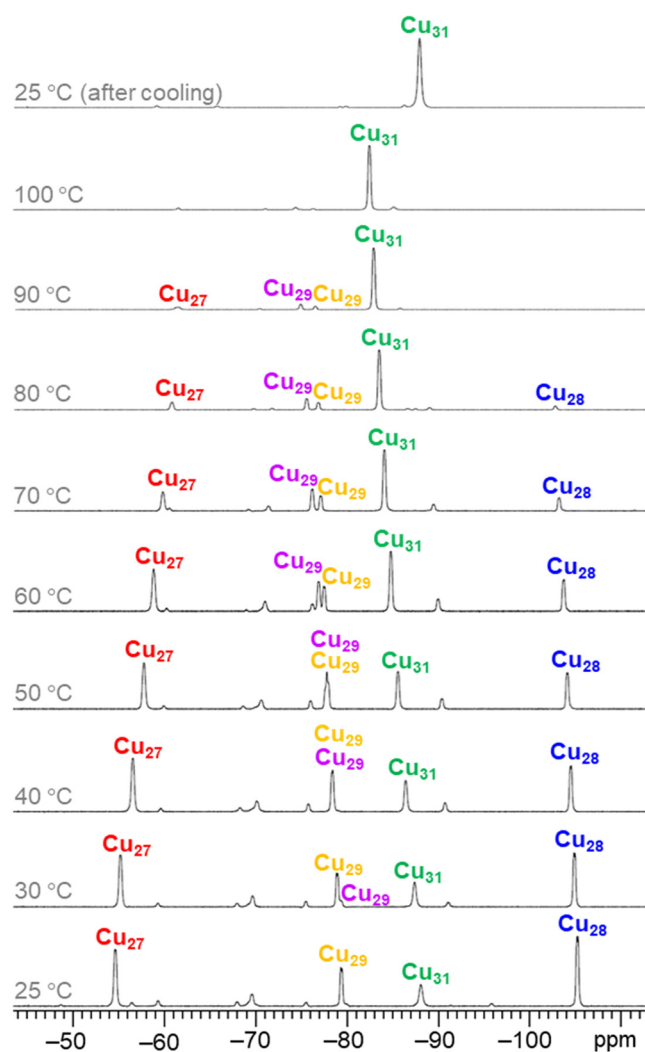


Figure 10. VT ^{19}F NMR spectra (376 MHz, $\text{DMSO-}d_6$) of the as-synthesized Cu_nBeF_4 ($n = 27\text{--}32$) nanojar mixture. Color code for the Cu_{29} nanojars: yellow, Cu_{7+13+9} ; magenta, Cu_{8+13+8} .

degradation products or a BaBeF_4 precipitate indicates that the $\text{Cu}_{27}\text{--Cu}_{30}$ species rearrange into the stable $\text{Cu}_{31}\text{BeF}_4$. This result is in agreement with the observation that $\text{Cu}_{31}\text{BeF}_4$ is the only major nanojar species obtained when Pb^{2+} ions are added during nanojar synthesis (see synthesis section above). Interestingly, when the experiment is conducted under homogeneous conditions using barium dioctyl sulfosuccinate [$\text{Ba}(\text{DOSS})_2$], which is soluble in 2-MeTHF together with the nanojar mixture, ESI-MS(−) indicates that the solution contains mostly the $\text{Cu}_{27}\text{BeF}_4$ and $\text{Cu}_{29}\text{BeF}_4$ species with reduced amounts of $\text{Cu}_{28}\text{BeF}_4$ and $\text{Cu}_{31}\text{BeF}_4$ and increased amounts of $\text{Cu}_{30}\text{BeF}_4$ and $\text{Cu}_{32}\text{BeF}_4$ (Figure S2c). Again, the absence of a BaBeF_4 precipitate or nanojar degradation products indicates a strong binding of the BeF_4^{2-} ion by nanojars.

Liquid–Liquid Extraction of BeF_4^{2-} from Water into Organic Solvents. Although the hydration energy of the BeF_4^{2-} ion has not been reported, based on its size and charge, BeF_4^{2-} is expected to have a fairly large value comparable to that of SO_4^{2-} ($\Delta G_h^\circ = -1064 \text{ kJ/mol}$).⁴⁴ Therefore, the extraction of BeF_4^{2-} from water into an organic solvent, as in the case of other highly hydrophilic anions, is anticipated to be challenging. BeF_4^{2-} extraction experiments were conducted by

stirring an aqueous $(\text{Bu}_4\text{N})_2\text{BeF}_4$ solution mixed with nanojar ingredients [$\text{Cu}(\text{NO}_3)_2$, pyrazole, and Bu_4NOH] in the water-immiscible solvent 2-MeTHF. ESI-MS shows that the same nanojar mixture is obtained as when THF was used for organic solvent (Figure S3). After separation of the organic layer, the aqueous layer was tested for BeF_4^{2-} by the addition of $\text{Ba}(\text{NO}_3)_2$. No precipitate was observed, whereas a control experiment led to the immediate precipitation of BaBeF_4 upon the addition of $\text{Ba}(\text{NO}_3)_2$. Similarly, extraction of BeF_4^{2-} from water into *n*-heptane was also demonstrated, by employing 4-octylpyrazole, which allows for dissolution of the nanojar in the hydrophobic aliphatic solvent. The extracted BeF_4^{2-} can be recovered from the organic layer by stripping with a dilute HNO_3 solution. As shown earlier,^{28,31} acidity leads to the breakdown of nanojars, resulting in the release of the incarcerated anion. Indeed, the addition of $\text{Ba}(\text{NO}_3)_2$ to the stripping solution after stirring it together with the organic layer causes the precipitation of insoluble BaBeF_4 .

3. CONCLUSIONS

We have studied for the first time the supramolecular binding and extraction of the highly toxic tetrafluoroberyllate anion from water by using nanojars as anion-binding agents. Mass spectrometry, NMR spectroscopy, and X-ray crystallography methods indicate that nanojars of different sizes, $[\text{BeF}_4\text{C}\{\text{Cu}(\text{OH})(\text{pz})\}_n]$ (Cu_nBeF_4 ; $n = 27\text{--}32$), all bind the BeF_4^{2-} ion at ambient temperature, whereas only the most robust $\text{Cu}_{31}\text{BeF}_4$ nanojar survives at 150 °C in a DMSO solution. $\text{Cu}_{31}\text{BeF}_4$ is also the most resistant nanojar to acidity because it is the only species observed (along with traces of $\text{Cu}_{32}\text{BeF}_4$) when slightly acidic $\text{Pb}^{2+}(\text{aq})$ is added to the reaction mixture during synthesis.

The observation of only one set of pyrazolate and OH proton peaks for each constituent Cu_x ring ($x = 6\text{--}14$, except 11) in the ^1H NMR spectra indicates high symmetry, which points to a fluxional structure of nanojars in solution. ^{19}F NMR spectroscopy reveals that the position of the incarcerated BeF_4^{2-} anion in the cavity of nanojars is also dynamic because only one F signal is observed for each Cu_nBeF_4 species. Characterization of the Cu_nBeF_4 nanojars by ^9Be NMR provides the first examples of paramagnetic ^9Be NMR spectra and, together with ^{19}F NMR, allows for the unprecedented direct probing of the incarcerated anion in nanojars.

Single-crystal X-ray diffraction reveals a novel nanojar structure, $[\text{BeF}_4\text{C}\{\text{Cu}(\text{OH})(\text{pz})\}_{9+14+9}]^{2-}$ ($\text{Cu}_{32}\text{BeF}_4$), along with the structures of $[\text{BeF}_4\text{C}\{\text{Cu}(\text{OH})(\text{pz})\}_{8+14+9}]^{2-}$ ($\text{Cu}_{31}\text{BeF}_4$) and $[\text{BeF}_4\text{C}\{\text{Cu}(\text{OH})(\text{pz})\}_{6+12+10}]^{2-}$ ($\text{Cu}_{28}\text{BeF}_4$). $\text{Cu}_{32}\text{BeF}_4$ has a unique structure among nanojars, both in terms of the molecular structure, which features distinct taco-shaped side rings and a saddle-shaped central ring, and in terms of the crystal structure, which features helical packing of nanojar units along 2_1 screw axes, leading to a chiral space group. The three crystal structures reiterate that the nanojar cavity has multiple configurations available for anion binding, with three different positions of the anion observed in $\text{Cu}_{32}\text{BeF}_4$ (major component, 60%; minor components, approximately 20% each). This shows that while in the solution phase nanojars can adopt different conformations, the incarcerated anion can bind in different ways even in one given nanojar conformation in the solid state (the only disorder in the structure of the Cu_{32} nanojar is a minor, 9° flip of one single pyrazolate unit).

In the absence of other viable methods, the BeF_4 binding strength of nanojars was assessed using competition experiments with Ba^{2+} , both in a heterogeneous setup using aqueous barium nitrate and a nanojar solution in 2-MeTHF and in a homogeneous setup using a solution of barium dioctyl sulfosuccinate and nanojars in 2-MeTHF. In both cases, no precipitation of the insoluble BaBeF_4 or the formation of any nanojar breakdown products is observed, indicating a strong binding of BeF_4^{2-} by nanojars. The transformation of smaller nanojars into $\text{Cu}_{31}\text{BeF}_4$ when aqueous Ba^{2+} is used emphasizes once again that Cu_{31} is the most stable nanojar with BeF_4^{2-} . Consequently, BeF_4^{2-} was successfully extracted from water into both the biorenewable, green solvent 2-MeTHF and the highly hydrophobic, aliphatic solvent *n*-heptane, from which it can be recovered by stripping with a dilute acid. Thus, it is shown that nanojars are excellent binding and extracting agents not only for oxoanions but also for fluoroanions.

4. EXPERIMENTAL SECTION

Warning! Be metal and its compounds are extremely toxic and carcinogenic if inhaled, swallowed, or in contact with skin. HF is highly corrosive and toxic. Appropriate precautions should be taken while handling and disposing of all Be-containing materials.

General Procedures. All commercially available chemicals were used as received. Deionized water was freshly boiled and cooled to room temperature under nitrogen gas. 4-Octylpyrazole was prepared as described earlier.²⁷ Barium dioctyl sulfosuccinate was obtained by mixing aqueous solutions containing sodium dioctyl sulfosuccinate and barium nitrate, respectively (in a 2:1 molar ratio), followed by filtration and drying. The synthesis and reactions of nanojars were carried out under an N_2 atmosphere. NMR spectra were collected on a Jeol JNM-ECZS (400 MHz) instrument, using 0.43 M BeSO_4 in water as an external standard in a coaxial NMR tube ($\delta = 0.00$ ppm) for the ^9Be NMR spectra (56 MHz) and $\text{C}_6\text{H}_5\text{CF}_3$ as an internal standard ($\delta = 0.00$ ppm; samples were spiked with 5 μL of a 2.0 mM $\text{C}_6\text{H}_5\text{CF}_3$ solution in $\text{DMSO}-d_6$) for the ^{19}F NMR spectra (376 MHz).

Synthesis of Sodium Tetrafluoroberyllate (Na_2BeF_4). A piece of Be metal (4.067 g, 0.4514 mol) was placed in water (50 mL) in a Teflon beaker cooled with an ice bath, and a solution of HF (40.6% in water, 80.0 mL, $d = 1.15$ g/mL, 1.87 mol) was added in small portions over 3 h with extreme caution in order to avoid overheating and excessive effervescence. To the resulting solution of tetrafluoroberyllic acid (H_2BeF_4) was added a solution of NaOH (38.230 g, 0.9558 mol) in water (100 mL) in small portions, under stirring, until a final pH of ~ 7 was reached. A colorless, crystalline precipitate was obtained (the solubility of Na_2BeF_4 is considerably reduced by the presence of NaF, whereas the solubility of NaF is little affected by Na_2BeF_4),⁴³ which was stirred for 5 h in the mother liquor, then filtered out, quickly rinsed with two 50 mL portions of ice-cold water, and dried in air overnight and then at 135 $^\circ\text{C}$ for 4 h. Yield: 56.417 g (95%). Purification was carried out by recrystallization from hot water. Solubility in water (g/100 mL): 1.33 (0 $^\circ\text{C}$), 1.44 (20 $^\circ\text{C}$), 2.73 (90 $^\circ\text{C}$).^{42,45} ^9Be NMR (56 MHz, D_2O): δ 0.58 (quint, $J_{\text{Be-F}} = 34$ Hz). ^{19}F NMR (376 MHz, D_2O): δ -61.78 (s, F^-), -107.01 (q, $[\text{BeF}_4]^{2-}$, $J_{\text{Be-F}} = 34$ Hz), -108.49 (q, $[\text{BeF}_3(\text{H}_2\text{O})]^-$, $J_{\text{Be-F}} = 37$ Hz).

Synthesis of Lead Tetrafluoroberyllate (PbBeF_4). A solution of $\text{Pb}(\text{NO}_3)_2$ (11.335 g, 34.22 mmol) in water (200 mL) was slowly added to a solution of Na_2BeF_4 (4.483 g, 34.22 mmol) in water (300 mL) under vigorous stirring. A white precipitate formed, which was stirred overnight, then filtered out, washed thoroughly with water, and dried in air overnight and then at 135 $^\circ\text{C}$ for 4 h. Yield: 5.722 g (57%).

Synthesis of Copper Tetrafluoroberyllate ($\text{CuBeF}_4 \cdot 5\text{H}_2\text{O}$). A solution of H_2BeF_4 was prepared as described above, from a piece of Be metal (2.384 g, 0.2646 mol) and HF (40.6% in water, 45.5 mL, $d = 1.15$ g/mL, 1.06 mol). To the resulting solution of H_2BeF_4 was added

$\text{Cu}_2\text{CO}_3(\text{OH})_2$ (29.6 g, 0.134 mmol) under stirring, in small portions (strong effervescence!). The excess $\text{Cu}_2\text{CO}_3(\text{OH})_2$ was filtered out, and the blue solution was concentrated by slow evaporation. $\text{CuBeF}_4 \cdot 5\text{H}_2\text{O}$ was obtained as large, blue crystals, which were removed from the solution by decantation and dried in air. Yield: 51.495 g (81%). ^9Be NMR (56 MHz, $\text{DMSO}-d_6$): δ 0.82 (s). ^{19}F NMR (376 MHz, $\text{DMSO}-d_6$): δ -67.24 (F^-), -101.87 (s, $[\text{BeF}_4]^{2-}$), -108.25 (s, $[\text{BeF}_3(\text{H}_2\text{O})]^-$).

Synthesis of Tetrabutylammonium Tetrafluoroberyllate $[(\text{Bu}_4\text{N})_2\text{BeF}_4 \cdot x\text{H}_2\text{O}]$. In a Teflon beaker, a solution of HF (40% in water, 3.86 mL, $d = 1.15$ g/mL, 88.8 mmol) was added in small portions under stirring to a solution of Bu_4NOH (1 M in water, $d = 1.00$ g/mL, 11.513 g, 44.4 mmol). Then, Be powder (200 mg, 22.2 mmol) was added in small portions to avoid excessive effervescence. The resulting clear colorless solution was evaporated, and the residue was dried under high vacuum to afford the product in quantitative yield (13.422 g; contains 5.74% water; $x = 1.93$). ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 3.17 (m, 8H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.56 (m, 8H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.30 (m, 8H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 0.92 (t, 12H, $J = 7.4$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). ^{13}C NMR (101 MHz, $\text{DMSO}-d_6$): δ 57.5, 23.1, 19.2, 13.5. ^9Be NMR (56 MHz, $\text{DMSO}-d_6$): δ -0.54 (s). ^{19}F NMR (376 MHz, $\text{DMSO}-d_6$): δ -95.61 (s).

Synthesis of $(\text{Bu}_4\text{N})_2[\text{BeF}_4\{\text{Cu}(\text{OH})(\text{pz})\}_n]$ (Cu_nBeF_4 ; $n = 27-32$). $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ (2.0000 g, 8.60 mmol), pyrazole (0.5854 g, 8.60 mmol), and $(\text{Bu}_4\text{N})_2\text{BeF}_4 \cdot x\text{H}_2\text{O}$ ($x = 1.93$; 5.1333 g, 8.60 mmol) were dissolved in THF (50 mL) in a 100 mL three-neck round-bottomed flask equipped with a pressure-equalizing addition funnel and a stir bar. Bu_4NOH (1 M in water, 17.20 mL, 17.20 mmol) was added dropwise from the addition funnel to the reaction solution under stirring. The deep-blue solution was cannulated into water (500 mL) under stirring. The blue precipitate was filtered off, washed thoroughly with water, and dried under high vacuum to afford a dark-blue powder. Yield: 1.1790 g ($\sim 82\%$). ESI-MS(-): m/z 2035, $\text{Cu}_{27}\text{BeF}_4$; m/z 2109, $\text{Cu}_{28}\text{BeF}_4$; m/z 2183, $\text{Cu}_{29}\text{BeF}_4$; m/z 2257, $\text{Cu}_{30}\text{BeF}_4$; m/z 2331, $\text{Cu}_{31}\text{BeF}_4$; m/z 2404, $\text{Cu}_{32}\text{BeF}_4$. ESI-MS(+): m/z 242, Bu_4N^+ .

Fractionation of $(\text{Bu}_4\text{N})_2[\text{BeF}_4\{\text{Cu}(\text{OH})(\text{pz})\}_n]$ (Cu_nBeF_4 ; $n = 27-32$). A mixture of tetrafluoroberyllate nanojars (0.1875 g) was dissolved in toluene (2.5 mL) with sonication. A deep-blue, clear solution was obtained. Upon standing for 48 h, a dark-blue precipitate formed. The solid was filtered out, washed with toluene, and dried under high vacuum to give 0.0888 g of dark-blue powder. The filtrate was evaporated under reduced pressure and dried under high vacuum to afford 0.0987 g of dark-blue powder. ESI-MS and ^1H NMR analyses showed that the precipitate consists almost exclusively of $\text{Cu}_{27}\text{BeF}_4$ and $\text{Cu}_{28}\text{BeF}_4$ with only traces of other nanojar sizes (Figure 1B), whereas the product obtained after evaporation of the filtrate contains mostly $\text{Cu}_{29}\text{BeF}_4$ and $\text{Cu}_{31}\text{BeF}_4$ nanojars together with small amounts of $\text{Cu}_{27}\text{BeF}_4$ and $\text{Cu}_{28}\text{BeF}_4$ and traces of other nanojar sizes (Figure 1C).

Synthesis of $(\text{Bu}_4\text{N})_2[\text{BeF}_4\{\text{Cu}(\text{OH})(\text{pz})\}_{31}]$ ($\text{Cu}_{31}\text{BeF}_4$). $\text{CuBeF}_4 \cdot 5\text{H}_2\text{O}$ (10.000 g, 41.908 mmol), pyrazole (2.853 g, 41.91 mmol), NaOH (3.282 g, 82.05 mmol), Bu_4NOH (1 M in water, 2.920 g, 2.920 mmol), and PbBeF_4 (5.722 g, 19.58 mmol) were stirred in THF (200 mL) for 3 days. The deep-blue solution was filtered, the solvent was evaporated, and the blue residue was dried under high vacuum. Yield: 6.836 g ($\sim 98\%$). ESI-MS(-): m/z 2331, $\text{Cu}_{31}\text{BeF}_4$; m/z 2404 (traces), $\text{Cu}_{32}\text{BeF}_4$. ESI-MS(+): m/z 242, Bu_4N^+ .

Competitive Anion Binding under Heterogeneous Conditions. Cu_nBeF_4 ($n = 27-32$, 0.1213 g) was dissolved in 2-MeTHF (25 mL) to give a clear, blue solution. A total of 20 mL of this solution (0.02 mmol of Cu_nBeF_4) was then cannulated over a solution of $\text{Ba}(\text{NO}_3)_2$ (0.0104 g, 0.04 mmol) in water (20 mL) contained in a 100 mL three-neck round-bottomed flask equipped with a stir bar. After vigorous stirring for 1 h, the aqueous and organic layers were separated and 2-MeTHF was removed under high vacuum, leaving behind a dark-blue residue. The remainder of the original nanojar solution (5 mL) was kept as a control. The control and organic layer were characterized by ESI-MS (Figure S2).

Competitive Anion Binding under Homogeneous Conditions. Cu_nBeF_4 ($n = 27\text{--}32$, 0.0972 g, 0.02 mmol) and $\text{Ba}(\text{DOSS})_2$ (0.0198 g, 0.02 mmol) were dissolved in 2-MeTHF (20 mL) to give a clear, blue solution. A control solution was prepared by dissolving Cu_nBeF_4 ($n = 27\text{--}32$, 0.0486 g, 0.01 mmol) in 10 mL of 2-MeTHF. The two solutions were stirred for 1 h, and then aliquots were taken from each for ESI-MS analysis (Figure S2).

Liquid–Liquid Extraction of BeF_4^{2-} from Water into 2-MeTHF and *n*-Heptane. $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ (0.4498 g, 1.93 mmol) and pyrazole (0.1316 g, 1.93 mmol) were dissolved in 2-MeTHF (50 mL) to obtain a clear, blue solution. $(\text{Bu}_4\text{N})_2\text{BeF}_4 \cdot x\text{H}_2\text{O}$ ($x = 1.93$, 0.0398 g, 0.0658 mmol) dissolved in CH_3CN (3 mL) was added into water (50 mL). The blue solution was added dropwise under stirring to the aqueous solution of $(\text{Bu}_4\text{N})_2\text{BeF}_4$ and Bu_4NOH (1 M in water, 3.87 mL, 3.87 mmol). The deep-blue organic layer was separated from the clear, colorless aqueous layer using a separatory funnel. The aqueous layer was tested for the presence of tetrafluoroberyllate by the addition of $\text{Ba}(\text{NO}_3)_2$ (0.0174 g, 0.0666 mmol). After stirring, barium nitrate completely dissolved, and the aqueous layer remained unchanged (clear, colorless). A control experiment using a clear solution of $(\text{Bu}_4\text{N})_2\text{BeF}_4 \cdot x\text{H}_2\text{O}$ ($x = 1.93$, 0.0398 g, 0.0658 mmol) in water (50 mL) produced a white precipitate (BaBeF_4) immediately upon the addition of $\text{Ba}(\text{NO}_3)_2$ (0.0174 g, 0.0666 mmol). Extraction from water to heptane was carried out similarly by using 4-octylpyrazole (0.348 g, 1.93 mmol) instead of pyrazole. The extracted BeF_4^{2-} was stripped from the organic layer by stirring with a dilute aqueous solution of HNO_3 (15 mL, 0.333 mmol) for 1 h. After separation of the organic and aqueous layers, a solution of $\text{Ba}(\text{NO}_3)_2$ (17.4 mg, 0.0666 mmol) in water was added to the aqueous layer, causing the immediate precipitation of BaBeF_4 .

Mass Spectrometry. Mass spectrometry analysis of the nanojars was performed with a Waters Synapt G1 HDMS instrument, using electrospray ionization. Solutions of $10^{-4}\text{--}10^{-5}$ M were prepared in CH_3CN . Samples were infused by a syringe pump at 5 $\mu\text{L}/\text{min}$, and nitrogen was supplied as the nebulizing gas at 500 L/h. The electrospray capillary voltage was set to -2.5 or $+2.5$ kV, respectively, with a desolvation temperature of 110 $^\circ\text{C}$. The sampling and extraction cones were maintained at 40 and 4.0 V, respectively, at 80 $^\circ\text{C}$.

X-ray Crystallography. Single crystals were grown from Cu_nBeF_4 ($n = 27\text{--}32$) solutions at room temperature by pentane vapor diffusion into a 1,2-dichlorobenzene solution in the presence of 1,3,5-trichlorobenzene (1), by heptane vapor diffusion into a chlorobenzene solution in the presence of 1-chloro-2,4-dinitrobenzene (2), and from a toluene solution upon standing (3). Once removed from the mother liquor, the crystals are very sensitive to solvent loss at ambient conditions and were mounted quickly under a cryostream (150 K) to prevent decomposition. X-ray diffraction data were collected from a single crystal mounted atop a MiTeGen micromesh mount under Fomblin oil with a Bruker AXS D8 Quest diffractometer with a Photon III C14 charge-integrating and photon-counting pixel array detector (CPAD) using graphite-monochromated $\text{Cu K}\alpha$ ($\lambda = 1.54178$ Å) radiation (for 1 and 3) and a Bruker AXS D8 Quest diffractometer equipped with a Photon II CPAD using graphite-monochromated $\text{Mo K}\alpha$ ($\lambda = 0.71073$ Å) radiation (for 2). The data were collected using APEX3,⁴⁶ integrated using SAINT,⁴⁷ and scaled and corrected for absorption and other effects using SADABS.⁴⁸ The structures were solved by employing direct methods using ShelXS⁴⁹ and refined by full-matrix least squares on F^2 using ShelXL.⁵⁰ H atoms in C–H were placed in idealized positions and refined using the riding model. Further refinement details and thermal ellipsoid plots are provided in Figures S4–S6.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem.2c01198>.

Additional data for mass spectrometry, X-ray crystallography, and ^1H NMR spectroscopy (PDF)

Accession Codes

CCDC 2163988–2163990 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

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