

NMR Spectroscopic Evidence for Magnetically Induced Ring Currents in All-Metal-Aromatic $[\text{Bi}_4]^{4+}$

Avijit Maiti, Jie Zhang, Ravi Yadav, Matthias Heinrich, Luca Bischof, Adrian Ellinger, Manuel Schmitt, Rüdiger Klingeler, Florian Weigend,* and Lutz Greb*

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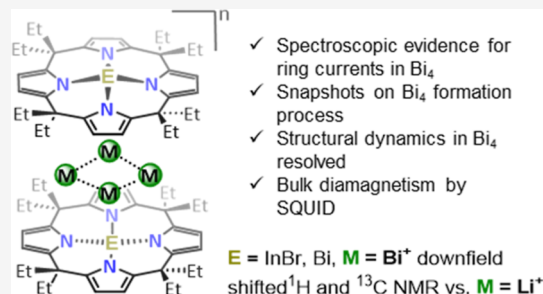


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ABSTRACT: Experimental assignment of aromaticity in all-metal systems remains challenging, particularly for heavy-element clusters, where local magnetic effects can obscure signatures of circular electron delocalization. Here, we investigate a supramolecularly stabilized, formally tetracationic $[\text{Bi}_4]^{4+}$ ring by combining structurally meaningful reference compounds, solid- and solution-state NMR spectroscopy, SQUID magnetometry, and exact two-component relativistic calculations. Comparison with an isostructural $[\text{Li}_4\text{Br}]^{3+}$ -encapsulated analogue and a binuclear Bi(III) reference compound disentangles global ring-current effects from local heavy-atom deshielding and ligand-specific conformational effects. On this basis, the unusually downfield-shifted ^1H and ^{13}C NMR signals observed for the Bi_4 -containing species provide direct spectroscopic evidence for magnetically induced ring currents in the $[\text{Bi}_4]^{4+}$ core. By contrast, bulk magnetic measurements do not reveal significant diamagnetic exaltation, indicating that this quantity is not a resolved descriptor of aromaticity in these systems. Stoichiometric studies further identify chemically competent intermediates that provide mechanistic snapshots of $[\text{Bi}_4]^{4+}$ ring formation. Complementary calculations support the assignment of a magnetically responsive, σ -delocalized $[\text{Bi}_4]^{4+}$ core, reproduce a rare spectroscopically observed puckering motion of the rhomboidal $[\text{Bi}_4]^{4+}$, and underscore the critical role of spin–orbit coupling on electronic structure and dynamics. Overall, this work moves the discussion of aromaticity from predominantly computational assignment toward experimentally benchmarked analysis in the heavy-element and all-metal regime.



INTRODUCTION

The question of whether aromaticity can arise in frameworks composed entirely of metal atoms has attracted considerable attention in recent years.¹ Beyond its conceptual appeal, this line of inquiry explores how one of chemistry's most influential bonding paradigms can be transferred into regions of the periodic table that are substantially distinct from its carbon-based origins. At the same time, all-metal aromaticity remains challenging to define and assess.² As in the long-established chemistry of carbon aromatics, its assignment cannot rest on a single descriptor, but instead demands for critical evaluation against the commonly invoked structural, electronic, energetic, and magnetic criteria of aromaticity.³ In classical organic compounds, energetic and structural criteria have been applied successfully, but they require comparison with chemically meaningful localized reference structures. For homoatomic metal rings, however, such reference states are often chemically inaccessible or ill-defined, rendering these criteria far less straightforward to apply. Accordingly, magnetic response properties remain as one of the most direct routes to assessing aromaticity,⁴ with spectroscopic evidence for magnetically induced ring currents constituting one of its most compelling manifestations.⁵ In organic aromatics, such ring currents are readily detected by NMR spectroscopy through characteristic

shielding patterns: nuclei located at the outer perimeter of the ring typically experience deshielding and appear downfield, while nuclei above the delocalization zone are high-field shifted (Figure 1a). Analogous experimental signatures remain exceptionally scarce for all-metal systems.⁶ A central obstacle is not merely spectroscopic sensitivity, but the lack of suitable reference compounds that preserve the relevant molecular framework while selectively removing the delocalized ring-current contribution.

Without such comparators, NMR features cannot be interpreted unambiguously, and claims of all-metal aromaticity have therefore relied heavily on computational tools such as nucleus-independent chemical shifts (NICS), gauge-including magnetically induced currents (GIMIC), and related analyses.^{3,7} Although these approaches have enabled undeniable progress, their interpretation is not always straightforward, particularly in heavy-element systems. In such cases, strong

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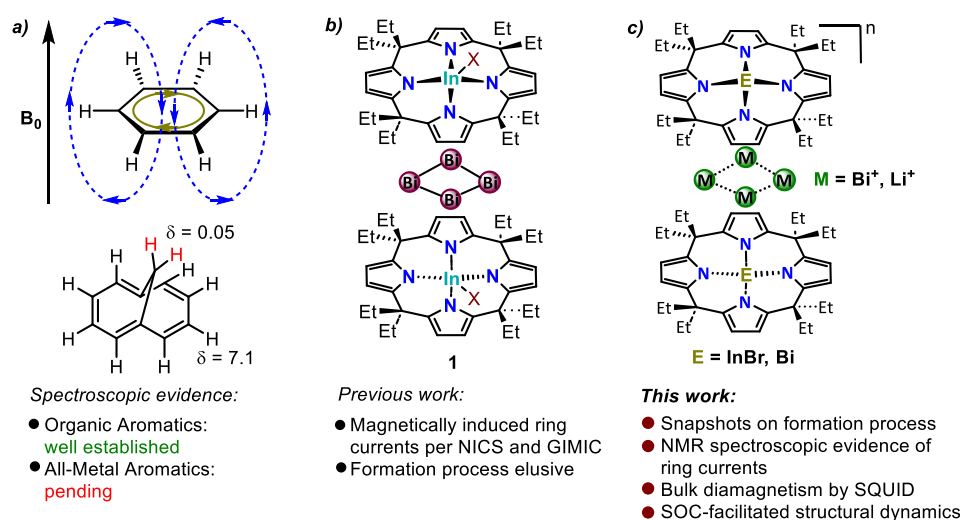


Figure 1. (a) Illustration of the ring-current effect associated with benzene aromaticity and its influence on proton chemical shifts in NMR spectroscopy. (b) Previously reported all metal σ aromatic $[\text{Bi}_4]^{4+}$ encapsulated by two ethyl-calix[4]pyrrolo (EtCx)-indinate dianions. (c) Structures used in this work: the $[\text{Bi}_4]^{4+}$ ring encapsulated by two ethyl-calix[4]pyrrolo-bismuth anions and the $[\text{Li}_4\text{Br}]^{3+}$ cluster encapsulated by two ethyl-calix[4]pyrrolo (EtCx)-indinate dianion ligands.

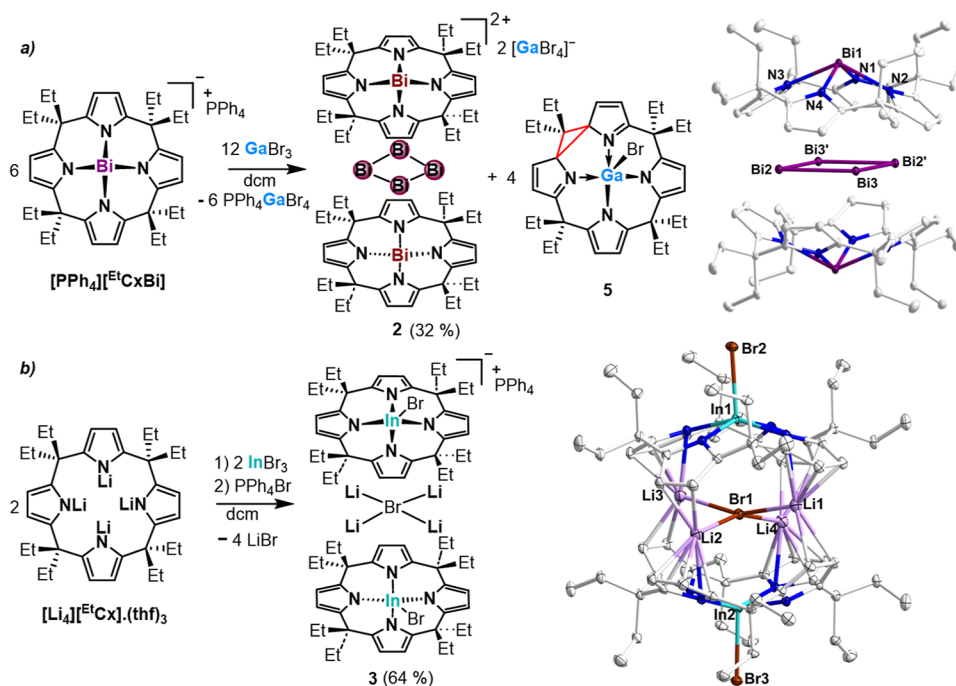


Figure 2. Synthesis of compounds (a) **2** and (b) **3**, including their scXRD-derived molecular structures.

local paramagnetic contributions, relativistic effects, and extensive orbital mixing can complicate the relationship between computed magnetic response and aromatic delocalization.⁸ Overall, these perturbations may rival or obscure the global magnetic consequences of electron delocalization, further underscoring the need for experimentally grounded observables that move beyond purely computational assessment. At the same time, explicit treatment of spin–orbit coupling (SOC) in experimentally accessible all-metal aromatic systems remains uncommon, despite its potentially decisive influence.⁹

Beyond local, nucleus-specific NMR effects, aromaticity may also be reflected in bulk magnetic properties. In classical organic systems, diamagnetic exaltation, that is, diamagnetic

susceptibilities exceeding the values predicted by additivity schemes such as Pascal's constants, has long been discussed as a macroscopic consequence of aromatic ring currents.¹⁰ By contrast, corresponding experimental data for all-metal aromatic compounds are only beginning to emerge.¹¹ SQUID studies revealed subtle diamagnetic exaltation, but at the same time underscored the considerable difficulty of extracting such small global magnetic signals with sufficient precision.¹²

Another limitation in the field concerns the formation processes of metal-only aromatic rings and clusters. Despite increasing interest in their electronic structures, insights into their assembly pathways remain scarce.¹³ The rich redox chemistry of such systems, their flexible bonding motifs, and

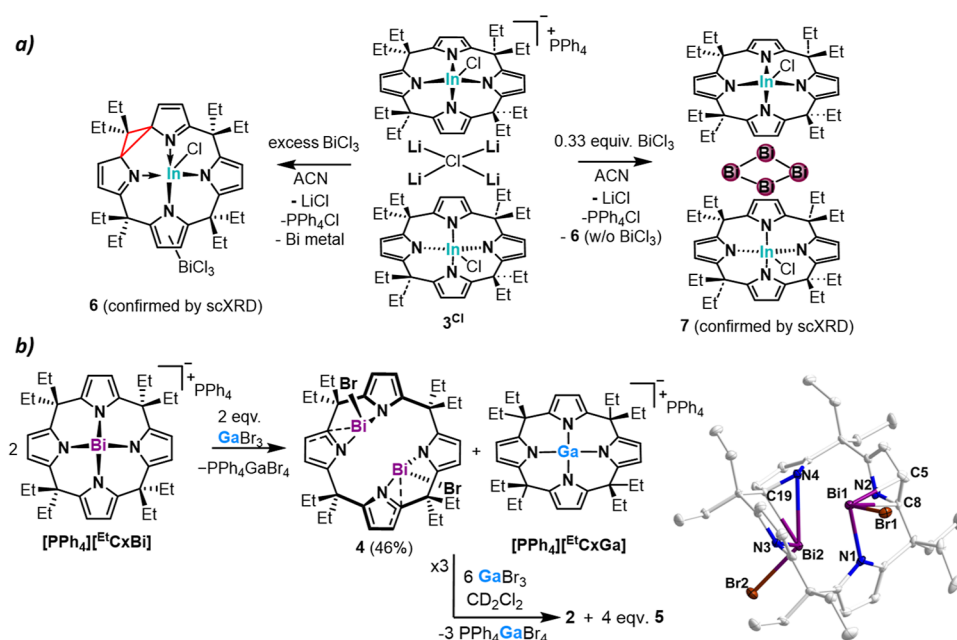


Figure 3. (a) Experimental support of the redox chemistry of $[\text{EtCxBi}]^{2-}$ (provided as 3^{Cl}) by the formation of **6** (in excess of BiCl_3) and **7** (in excess of 3^{Cl}). (b) Isolated intermediate **4** during the formation mechanism of **2**, along with the scXRD structure of **4**.

the frequent involvement of transient lower-nuclearity intermediates considerably complicate the mechanistic analysis. Consequently, the emergence of aromatic metal clusters is often rationalized only retrospectively, and structurally characterized intermediates remain rare. Finally, although structural dynamics and fluxionality are well-documented in metal clusters,¹⁴ such behavior has rarely been documented in all-metal aromatic species.

We recently reported a formally tetracationic, σ -aromatic $[\text{Bi}_4]^{4+}$ ring stabilized by supramolecular encapsulation between two ethyl-calix[4]pyrrolato ($[\text{EtCxBi}]^{2-}$)-indinate dianions (**1**, Figure 1b).¹⁵ GIMIC calculations pointed to the presence of a magnetically induced ring current in this compound, but definitive spectroscopic validation was precluded by insolubility and the absence of appropriate reference systems. At the same time, although the formation of the $[\text{Bi}_4]^{4+}$ core was presumed to proceed through a complex sequence of redox processes, a mechanistic picture remained vague.

In the present study, we address these issues through a combined mechanistic, spectroscopic, and magnetic analysis of the $[\text{Bi}_4]^{4+}$ platform (Figure 1c). First, we identify and characterize intermediates that provide mechanistic insights into the assembly of the $[\text{Bi}_4]^{4+}$ ring. Second, by employing carefully designed reference compounds and a soluble derivative of **1**, we provide direct ^1H and ^{13}C NMR spectroscopic evidence for magnetically induced ring currents in the $[\text{Bi}_4]^{4+}$ core. We further used high-sensitivity SQUID magnetometry to test whether this local aromatic response is reflected in a measurable bulk magnetic signature. Finally, exact two-component relativistic computations (i.e., including SOC) corroborate the experimental findings and account for a puckering motion of the $[\text{Bi}_4]^{4+}$ rhomboid. Taken together, these results move the discussion of all-metal aromaticity from predominantly computational assignment to experimentally benchmarked analysis in the heavy-element regime.

RESULTS AND DISCUSSION

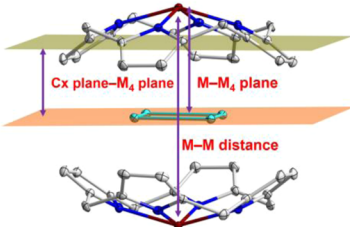
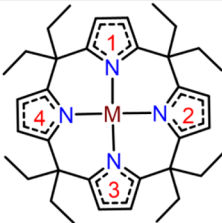
Design and Synthesis of Target and Reference Compounds

To establish experimentally grounded signatures of ring currents in the $[\text{Bi}_4]^{4+}$ platform, we first prepared a set of target and reference compounds designed to disentangle global aromatic response from local heavy-atom and ligand-based effects: the previously reported $[\text{Bi}_4]^{4+}$ containing species **1**, featuring two $[\text{EtCxBi}]^{2-}$ capping units;¹⁵ $[\text{Bi}_4]^{4+}$ containing species **2**, supported by two $[\text{EtCxBi}]^{2-}$ caps, and reference compound **3**, in which the $[\text{Bi}_4]^{4+}$ core is replaced by a $[\text{Li}_4\text{Br}]^{3+}$ unit (Figure 2). Compound **2** was synthesized by treating 1 equiv of $[\text{PPh}_4][\text{EtCxBi}]$ with two equiv of GaBr_3 in dry dichloromethane under inert conditions. The reaction mixture gradually darkened, and dark crystals of **2** developed from solution over several days at room temperature in 32% yield, alongside the two-electron-oxidized calix[4]pyrrolate as its gallium bromide complex **5** (Figure 2a). The $[\text{Li}_4\text{Br}]^{3+}$ reference compound **3** was obtained by the reaction of $[\text{EtCxBi}]^{2-}$ with InBr_3 in dichloromethane to give the anionic complex $[\text{EtCxBi}][\text{Li}_4\text{Br}][\text{EtCxBi}]$, followed by ion exchange with PPh_4Br , affording **3** in 64% yield (Figure 2b). An analogous reaction sequence with InCl_3 gave the isostructural chloride derivative 3^{Cl} .

MECHANISTIC INSIGHTS INTO THE FORMATION OF **1** AND **2**

Having these compounds at hand, we first revisited the formation mechanism of **1**.¹⁵ In our previous work, we proposed transmetalation of $[\text{PPh}_4][\text{EtCxBi}]$ with InBr_3 leading to a $[\text{EtCxBi}]^{2-}$ intermediate as the first step, which is then capable of reducing the released Bi(III) species. While direct structural evidence for such an $[\text{EtCxBi}]^{2-}$ intermediate was not available at that time, isolated species of type **3** now provided a means to evaluate this proposal. Indeed, the reaction of 3^{Cl} with an excess of BiCl_3 led to an oxidation of the

Table 1. Comparison of Structural Features of 1–3 and 4

Line	Cpd.	M–M	M–M' plane	Cx plane–M' plane			
1	1	7.508(9)	3.753(4)	2.481(8)			
2	2	8.208(8)	4.104(4)	2.495(8)			
3	3	6.741(9)	3.371(7)	2.249(7)			
			ring 1	ring 2	ring 3	ring 4	
4	2	Avg. C–C	1.390	1.391	1.394	1.395	
5		Avg. C–N	1.392	1.390	1.390	1.382	
6	3	Avg. C–C	1.391	1.393	1.399	1.399	
7		Avg. C–N	1.387	1.384	1.389	1.389	
8	4	Avg. C–C	1.393	1.398	1.412	1.416	
9		Avg. C–N	1.386	1.384	1.364	1.379	

calix[4]pyrrolato framework and crystallization of species 6 (Figure 3a, left), alongside the formation of elemental bismuth.

This observation supports that a $^{\text{Et}}\text{CxBiBr}$ dianion can serve as the reducing agent toward Bi(III). The poor yield of this reaction and the failure to observe a compound of type 1 under these conditions are not surprising but can be rationalized by the lack of remaining $^{\text{Et}}\text{CxBiBr}$ dianion that would template or capture any assembled, multinuclear Bi(I) intermediates. Consistent with this assumption, the formation of 7 was observed only when the reaction was conducted with 3^{Cl} in excess relative to BiCl_3 (Figure 3a, right). A refined scenario is therefore that the bowl-shaped $^{\text{Et}}\text{CxBiBr}$ dianion binds Bi(III) ions, positions them in proximity, and enables reduction by additional $^{\text{Et}}\text{CxBiBr}$ dianion equivalents, promoting Bi–Bi bond formation en route to 1.

Whereas this pathway appears plausible for the formation of 1, a distinct scenario emerged for the formation of 2 from a closer examination of the reaction between $[\text{PPh}_4][^{\text{Et}}\text{CxBi}]$ and GaBr_3 . Mixing the two reagents in a 1:1 ratio, instead of the 1:2 ratio used for synthesis of 2, gave rise to two $^{\text{Et}}\text{CxBi}$ -containing species in a 1:1 ratio, as judged by ^1H NMR spectroscopy. Preparative-scale isolation identified these as a new bismuth-containing species 4 and $[\text{PPh}_4][^{\text{Et}}\text{CxBi}]$,¹⁶ together with $\text{PPh}_4\text{GaBr}_4$ (Figure 3b). Single-crystal X-ray diffraction of 4 revealed the incorporation of two BiBr-units within the calix[4]pyrrolato scaffold, featuring metrical parameters consistent with other reported Bi(III)–N and Bi(III)–Br bonds.¹⁷ The relatively short Bi–C distances (Bi1–C5 = 2.522(5) Å and Bi2–C19 = 2.425(4) Å) were indicating additional π -interaction with the pyrrolates.¹⁸ Detection of 4 suggested a pathway distinct from the redox manifold observed for 1. In this scenario, the transmetalation of $[\text{EtCxBi}]^-$ with GaBr_3 occurs first, while the released $\text{Bi(III)Br}_3^{3-n+}$ fragment is incorporated into a remaining $[\text{EtCxBi}]^-$ anion. The redistribution of bromide between the two bismuths then gives 4, while the second equivalent of GaBr_3 is converted into GaBr_4^- . Interestingly, the mixture of 4 and $[\text{PPh}_4][^{\text{Et}}\text{CxBi}]$ remained stable for up to 4 days, in marked contrast to the near-complete formation of 2 over a comparable time scale when a 2-fold excess of GaBr_3 is employed (cf. Figure 2a). This observation suggests that $[\text{PPh}_4][^{\text{Et}}\text{CxBi}]$ alone is not sufficient to reduce 4, but instead acts as a reducing agent only in the presence of additional GaBr_3 . To probe this

hypothesis, isolated 4 was treated with 2 equiv of GaBr_3 in CD_2Cl_2 . The reaction gave a complex mixture by NMR spectroscopy, with no evidence for the formation of 2. By contrast, combining 4 with 2 equiv of GaBr_3 in the presence of $[\text{PPh}_4][^{\text{Et}}\text{CxBi}]$ immediately afforded a black precipitate. After washing with DCM, SCXRD analysis confirmed the formation of the $[\text{Bi}_4]^{4+}$ -containing product 2 (ESI, Section 1.2.6). These observations establish 4 as a viable intermediate and indicate that additional GaBr_3 is required, potentially to abstract bromide from 4, generating cationic, binuclear bismuth(III) species that can be reduced by $[\text{EtCxBi}]^-$.

In this reaction sequence, intermediate 4 might serve for positioning two Bi(III) atoms in proximity for subsequent reductive Bi–Bi bond formation. However, the participation of bowl-shaped $[\text{PPh}_4][^{\text{Et}}\text{CxBi}]$, analogous to the role proposed for the bowl-shaped $^{\text{Et}}\text{CxBiBr}$ dianion in formation of 1, cannot be excluded. Overall, these experiments do not establish the entire mechanism but provide mechanistic snapshots of two plausible and apparently distinct pathways, leading to the cationic all-metal rings through complex redox sequences.

Structural Comparison of Bi_4 -Containing and Reference Assemblies

To ensure that the NMR shifts discussed in the following section are not a consequence of trivial geometric or conformational differences, but reflect the nature of the encapsulated core, we first analyzed the solid-state structures of 1–3. Only most significant aspects are discussed here. In all three compounds, interaction with the encapsulated ions enforces an eclipsed arrangement of the two $^{\text{Et}}\text{CxBi}$ capping units $[\text{M} = \text{Bi or InBr}]$. The distances between the metal centers of the capping units (M–M), the central M'_4 plane (M– M'_4 plane), and the pyrrolato centroid plane (Cx plane– M'_4 plane) vary as expected with ion size, being larger for the Bi_4 containing 1 and 2, but smaller for the more compact Li^+ ions in 3 (Table 1). Analysis with Bröring's ProphyStruct tool reveal closely similar bowl-shaped, domed conformations of the calix[4]pyrrolato frameworks in all three cases (ESI, Section 2.3).¹⁹ Most importantly, the averaged C_α – C_β and C–N bond lengths within the pyrrolato subunits of 2 and 3 are comparable, arguing against significant ligand oxidation or charge transfer to the encapsulated core (Table 1, lines 4–7). This supports the formal assignment of a $[\text{Bi}_4]^{4+}$ unit in 2, and analogous conclusions hold for 1 (ESI, Section 1.2.8). Taken

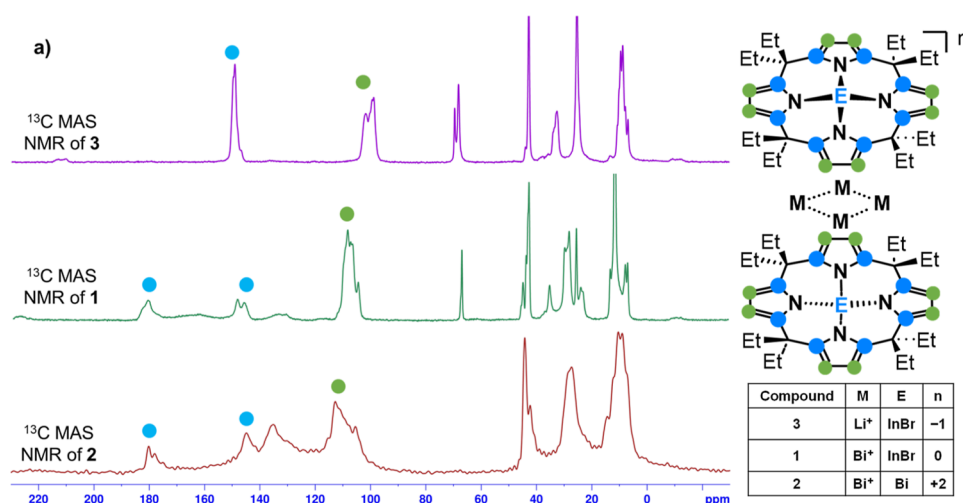


Figure 4. ^{13}C -MAS NMR spectra for compounds 1–3 at 14,000 Hz spinning rate.

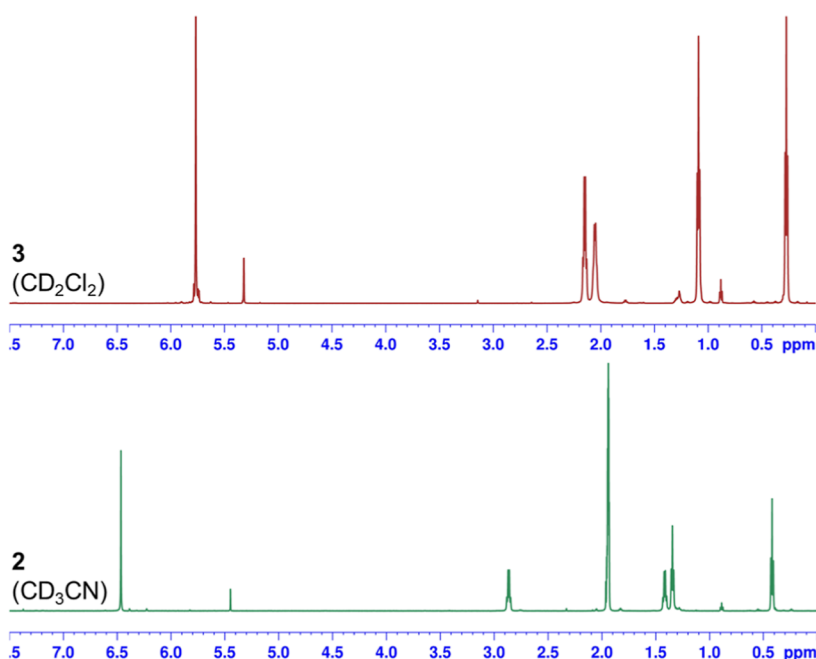


Figure 5. ^1H NMR spectra for compounds 2 and 3.

together, the structural similarity of 1–3 minimizes geometric and conformational variables in the spectroscopic comparison, allowing differences in NMR chemical shifts to be attributed primarily to the nature of the encapsulated core.

As an additional reference for the spectroscopic analysis, the structure of binuclear Bi(III) compound 4 was considered. In this case, the markedly shorter Bi–C contacts (2.522(5) Å to pyrrole β -carbon/2.425(4) Å to pyrrole α -carbon) compared to the corresponding distances in 1 (2.982(3) and 3.051(3) Å) and 2 (3.068(3) and 3.048(4) Å, α -carbon and β -carbon, respectively) indicate substantially stronger interaction between Bi and the pyrrolo units. Consistent with this, the comparison of the averaged C–C and C–N bond lengths in the pyrrole rings of 1–3 with those in 4 indicates partial dearomatization of the rings containing N2 and N4 in 4 (blue numbers in Table 1, lines 8/9). This difference becomes of importance during the interpretation of the NMR spectroscopic data discussed below.

NMR Evidence for Magnetically Induced Ring Currents

Having established the close structural similarity of 1–3 and the distinct local bonding situation in 4, their NMR spectroscopic properties were examined. Because 1 is insoluble in essentially all common organic solvent, solid-state MAS ^{13}C NMR was investigated first. In the $[\text{Bi}_4]^{4+}$ -containing compounds 1 and 2, the quaternary α -pyrrole carbon atoms give rise to unusual signals in the ^{13}C solid-state NMR spectra: one set in the expected pyrrole region at ca. 145 ppm and a second set at >178 ppm (Figure 4). By contrast, the corresponding carbon atoms in the $[\text{Li}_4\text{Br}]^{3+}$ -containing 3 appear as a single resonance at 149 ppm. The strongly downfield-shifted signal set at >178 ppm is striking and, to the best of our knowledge, unprecedented for any calix[4]-pyrrolo metal π -complex,²⁰ even for those containing very heavy metals such as gold (147 ppm),²¹ ruthenium (143 ppm),²² ytterbium (145 ppm),²³ or thorium (159 ppm).²⁴

To still exclude local effects from the individual Bi atoms as the origin of the pronounced downfield shift, we compared these data with those of **4**, which features structurally validated close Bi–C interaction. In **4**, the quaternary α -pyrrole carbon atoms resonate at 158.7 ppm in the ^{13}C NMR spectrum (CD_2Cl_2), which is substantially less downfield than in **1** and **2**. It should be noted that ^{13}C NMR signals of calix[4]pyrrolo ligands are shifting downfield also upon dearomatization.²⁵ Indeed, dearomatization is evident in **4** from its solid-state structure, but absent in **1** and **2** (vide supra). Accordingly, the influence of local Bi coordination, corrected for this effect, should be even smaller than that observed for **4**. Taken together, these comparisons indicate that neither local Bi coordination nor ligand-centered electronic perturbations can account for the extreme deshielding observed in the $[\text{Bi}_4]^{4+}$ -containing compounds. The observed signal splitting and pronounced downfield shift in **1** and **2** are therefore best explained by a magnetically induced deshielding effect associated with the $[\text{Bi}_4]^{4+}$ -ring current.⁵

In contrast to **1**, compound **2** provides a soluble derivative of the $[\text{Bi}_4]^{4+}$ system and thereby enables solution-state NMR studies. Although **2** remains insoluble in CH_2Cl_2 , it dissolves in acetonitrile. In CD_3CN , its integrity is maintained for up to 3 weeks, although slow partial conversion into a clean species exhibiting spectroscopic features analogous to those of the anion in $[\text{PPh}_4][^{\text{Et}}\text{CxBi}]$ is observed over time (ESI, Figures S31). We attribute this behavior to slow dissociation of an $[\text{EtCxBi}]^-$ capping unit from the $[\text{Bi}_4]^{4+}$ core, which becomes solvated in the donor solvent CD_3CN . Consistent with this interpretation, immediate dissociation of $[\text{EtCxBi}]^-$ was observed upon measuring **2** in the more strongly donating solvent DMSO (ESI, Figure S30). The fate of the $[\text{Bi}_4]^{4+}$ ring under these conditions remains unclear, but the sufficient stability of **2** in CD_3CN enabled direct comparison of the ^1H NMR spectrum with those of species **3** (Figure 5), as well as with **4** and $[\text{PPh}_4][^{\text{Et}}\text{CxBi}]$ (ESI, Figures S25–S31, Table S1). Most notably, compound **2** exhibits a markedly downfield-shifted resonance at 2.86 ppm, assigned to eight CH_2 groups for the ethyl groups—a chemical-shift range not previously observed for any $^{\text{Et}}\text{CxBi}$ -containing species. By comparison, the corresponding CH_2 signals appear at 2.16 ppm in **3**, 2.01 ppm in **4**, and 1.90 ppm in $[\text{PPh}_4][^{\text{Et}}\text{CxBi}]$, making explanations based solely on nearby metal centers or enforced ligand conformations implausible. Similar trends are also observed for the more distal CH_3 groups in the ethyl chains (ESI, Table S1).

Notably, the ^1H NMR signal pattern for **2** in solution indicates a higher symmetry (averaged) than that inferred from the solid-state NMR data. This signal averaging is further supported by comparing the solution and solid-state ^{13}C NMR spectra of **2** (see ESI, Section 1.2.9). In solution, the quaternary α -pyrrole carbon resonates as a single peak at 163.4 ppm, as determined by HMBC spectroscopy, in contrast to the two distinct ^{13}C NMR shift regions observed in the MAS NMR spectrum (180 and 145 ppm). These features are consistent with a low barrier dynamic process of the $[\text{Bi}_4]^{4+}$ rhomboid, which restores time-averaged symmetry on the NMR time scale.

Taken together, the combined solid- and solution-state NMR data indicate that neither local Bi coordination, ligand conformational effects, nor ligand-centered electronic perturbations are sufficient to account for the observed deshielding. The pronounced downfield shifts in **1** and **2** are therefore best

explained by a magnetically induced ring current effect associated with the $[\text{Bi}_4]^{4+}$ core. Moreover, in solution, structural dynamics were observed. All of these features are considered, refined, and supported by computations, as described in the following section.

Computational Section

To complement the experimental findings, we undertook computational analyses, focused at three questions: (1) whether the $[\text{Bi}_4]^{4+}$ unit retains the magnetic response expected for a σ -delocalized ring, (2) whether SOC influences this response, and (3) how the observed solution-state signal averaging in **2** can be explained. Because ring-current calculations had previously been reported only for **1**,¹⁵ the present study focuses on **2**, a more explicit analysis of SOC effects, and on computed NMR shifts.

Structure Optimizations

Geometric structures of the bare Bi_4^{4+} ring, **1**, **2**, and reference compound **3** were optimized at the DFT level using PBE,²⁶ together with dhf-TZVP basis sets²⁷ and corresponding effective core potentials (ECP),²⁸ as well as COSMO solvation for Bi_4^{4+} (see Supporting Information for details).²⁹ In addition, a hypothetical reference system **2**^{Xe} was generated from **2** by replacing the central Bi_4 rhombus with Xe atoms without further geometry optimization.

Aromaticity in the Bi_4 Units: Magnetic Criterion

Aromaticity according to the magnetic criterion was investigated for the bare Bi_4^{4+} ring and for the embedded Bi_4 unit in **2**, with a special focus on the influence of SOC. Magnetically induced current strengths were determined using both GIMIC³⁰ and the AMI (Ampère-Maxwell integration) procedure based on NICS(zz) values (ESI, Section 4).³¹ With the AMI approach, it is possible to quantify the influence of SOC by employing NICS(zz) obtained with and without SOC for the integration. Without SOC (i.e., ECP or SR-X2C), the current amounts to ~ 10 nA/T for bare Bi_4^{4+} (Table 2). When accounting for SOC, the current strength breaks down to ~ 1 nA/T. A similar sensitivity to SOC has recently been noted for an embedded Bi_3 ring.^{12b} For the GIMIC approach, currently only calculations at one-component level, i.e., without considering SOC, are possible. This yields a current of 9.98 nA/T, comparable to the SOC-free AMI values.

Table 2. Calculated Current Strengths for the Bi_4 Unit in Compound **2, and for Bare Bi_4^{4+} with Different Methods for Describing Relativity, with Different Ways of Integration (GIMIC, AMI) and, for the Composed System **2**, with Different Ways of Decomposing the Current in Contributions from Bi_4 and the Remainder: Via a Decomposition According to Basis Functions (“Bases”), a Spatial Profiling of the Current Plane (“Spatial”), and by Integrating the Difference of the Current Densities of the Entire System and the Corresponding “Empty” System Consisting of the Caps Only (“Caps”)**

integration	relativity	$[\text{Bi}_4]^{4+}$	2
AMI of NICS(zz), (caps for 2)	ECP	10.15	20.08
	SR-X2C	10.08	21.08
	SO-X2C	1.35	15.25
GIMIC, <i>spatial</i>	ECP	9.98	10.73
GIMIC, <i>bases</i>	ECP		12.06
GIMIC, <i>caps</i>	ECP		21.13

The situation is different for compound **2**. For this more complex structure, the current in the Bi_4 unit needs to be separated from that in the inherently aromatic calix[4]-pyrrolo caps. Within GIMIC, this can be done by choosing the upper and lower integration boundaries appropriately (“*spatial*” in Table 2, ESI, Section 4). In this way, one finds a current of 10.73 nA/T. Alternatively, the matrices for the electron density and density response may be decomposed according to the location of the basis set centers, similar to a Mulliken population analysis, as realized in a novel local implementation. This leads to a current strength of 12.06 nA/T (“*bases*” in Table 2). Further, this allows for a clearer visualization of the magnetically induced current density (MICD, Figure 6c, shown for **2**), indicating that the diatropic

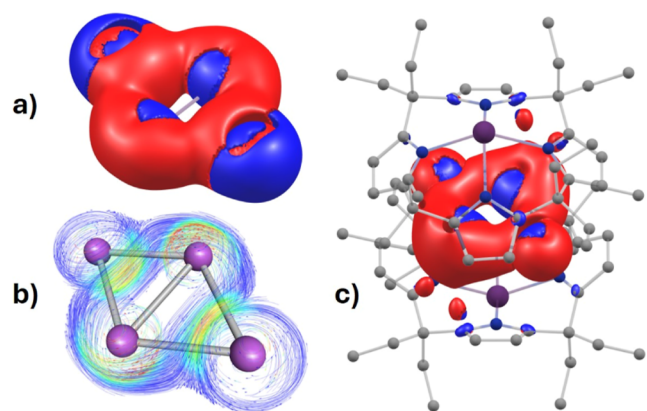


Figure 6. (a,b) Iso-surface and streamline plots of the MICD in Bi_4^{4+} . (c) Iso-surface plot of the contribution of the $\{\text{Bi}_4\}$ unit to the MICD in compound **2**. For the iso-surface plots red/blue color indicates diatropic/paratropic MICD, contours are drawn at ± 0.02 au.

current flows around the short diagonal of the Bi_4 rhombus (Bi^A atoms in Figure 7). Finally, one can obtain the current of

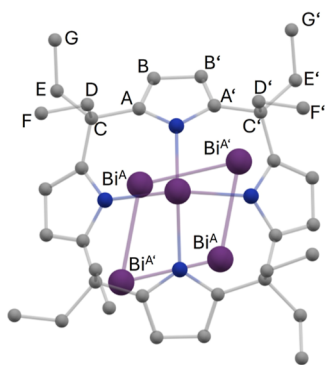


Figure 7. Labels for the individual carbon atom position, using **2** as an example. The second CxBi ligand is omitted for visual clarity. α -Pyrrole: A/A'; β -pyrrole: B/B'; meso: C/C'; axial Et-group: D/D' and F/F'; equatorial Et-group: E/E' and G/G'.

Bi_4 in **2** by calculating the difference of the entire system and a system consisting of the caps only (“*caps*” in Table 2). This technique has the advantage that it can also be applied to AMI, thereby allowing a qualitative assessment of the influence of SOC on the current in the Bi_4 ring in **2**.

Without SOC, the current of the Bi_4 unit in **2** calculated in this way is ~ 20 nA/T, again largely independent of the way of integration (AMI vs GIMIC) and the use of ECPs or SR-X2C.

However, in contrast to the current breakdown in bare Bi_4^{4+} , the influence of SOC on the current of Bi_4 in **2** is only moderate. If SOC is taken into account by employing NICS(zz) from a SO-X2C treatment in the AMI, it still amounts to ~ 15 nA/T. With all due caution, SOC tends to cause a decrease in the Bi_4 current in **2**, but not the entire breakdown as in bare Bi_4^{4+} . The origin of the markedly different SOC response of bare and embedded Bi_4^{4+} remains to be clarified, but the present calculations show that the supramolecular environment substantially moderates the collapse of the ring current seen for the isolated ring—in line with the spectroscopic findings.

NMR Shifts

Computed ^1H and ^{13}C NMR shifts at the two-component all-electron relativistic level reproduce the key experimental trends very well (see Tables S3–4, S6–S9). The most important ^{13}C NMR and ^1H NMR shifts are listed in Table 3 (for the labels of positions see Figure 7). Additionally, in Figure 8, the ^{13}C shifts of **2** are plotted versus those of **3** and 2^{Xe} . A very clear picture emerges from the data. The presence of the Bi_4 unit in **1** or **2** drastically increases the calculated ^{13}C shifts of the α -pyrrole carbon atoms A by ~ 50 ppm relative to reference compounds **3** or 2^{Xe} , while for the other positions (including A'), the changes are about 1 order of magnitude smaller. Interestingly, the largest shift is thus produced not at the carbon positions, which are closest to any bismuth atoms ($\text{Bi}^A \cdots \text{C}^{A'} = \text{avg. } 3.06 \text{ \AA}$), but at position that is close to the bismuth at the short diagonal ($(\text{Bi}^A \cdots \text{C}^A = \text{avg. } 3.10 \text{ \AA})$). These Bi^A are those the most involved in the computed diatropic ring current (cf. Figure 6b), corroborating that the observed unusual shift does not originate from the mere closeness of a bismuth atom, but from the magnetically induced ring current. The same holds for the computed ^1H NMR shifts, well reproducing the unusually downfield shifted equatorial CH_2 resonance for **2** at positions E/E' (2.9 ppm (exp) vs 3.1 ppm (comp)), underscoring the substantial shift of $+0.83/+0.48$ ppm for E/E' in the presences of the Bi_4 unit. The influence of SOC on the ^{13}C and ^1H NMR shifts was considered by repeating the computations at the scalar-relativistic SR-X2C/PBE/x2c-TZVP all-level (where SOC is neglected, Tables S8 and S9 and Figure S47). As the main result, we note that the presence of Bi_4 increases ^{13}C shifts at position A still by ~ 40 ppm, and ^1H shift at position E by 0.94 ppm, while at position E', the shifts are nearly unchanged (0.01 ppm). A detailed analysis of the effect of SOC on the other C atoms is shown in Figure S48, reflecting that the effect of SOC is relevant only for atoms showing distances of less than ~ 400 pm to the closest Bi atom.

Structural Dynamics in 2

Intrigued by the apparent D_{4h} signal averaging in the solution-state NMR spectra of **2**, we examined the mechanism of this dynamic process. Because the two capping ligands possess 4-fold rotational symmetry, a second degenerate minimum is obtained by exchanging the long and short diagonals of the Bi_4 rhombus. Interconversion between these minima could, in principle, occur either by rotation of the rhombus or via a square-like D_{4h} transition state. Exploratory calculations clearly identified the latter pathway, corresponding to a puckering motion of the $[\text{Bi}_4]^{4+}$ ring (Figure 9a). The importance of SOC emerges from inspection of MOs (without considering SOC) versus spinors (complex orbitals when considering SO coupling), for the quadratic puckering transition state of bare

Table 3. Selected Calculated ^{13}C and ^1H NMR Shifts (in ppm, w.r.t. SiMe_4) for the Compounds 1–3 and 2^{Xe} at Two-Component All-Electron Relativistic Level (i.e., Including SO Coupling)

		1		2		2^{Xe}		3	
		avg.		avg.		avg.		avg.	
Computed ^{13}C NMR shift									
α -pyrrole	A'	150.73	174.47	151.66	173.36	150.00	148.34	153.94	153.90
	A	198.21		195.06		146.37		153.87	
β -pyrrole	B'	105.41	105.76	110.45	111.53	117.96	115.34	102.74	102.76
	B	106.11		112.61		111.70		102.79	
Computed ^1H NMR shift									
β -pyrrole	B'	6.18	6.17	6.59	6.58	6.05	6.00	5.91	5.92
	B	6.17		6.57		5.96		5.93	
ethyl-CH ₂ (equat.)	E'	2.89	3.03	3.00	3.07	2.52	2.42	2.31	2.33
	E	3.16		3.17		2.34		2.34	
ethyl-CH ₃ (equat.)	G'	1.30	1.32	1.41	1.43	0.96	0.97	1.03	1.03
	G	1.34		1.44		0.98		1.03	

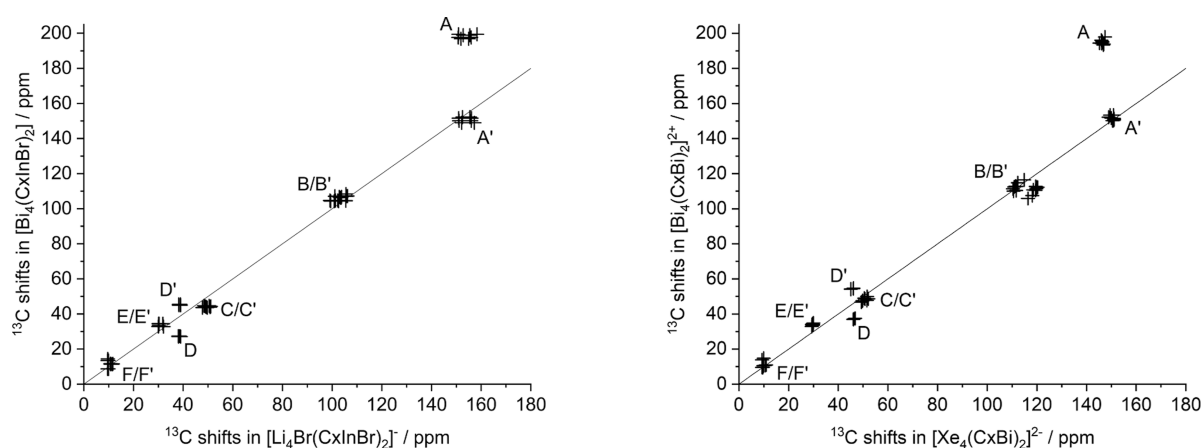


Figure 8. Comparison of ^{13}C shifts of (a) 1 versus 3 and (b) 2 versus 2^{Xe} , calculated at the 2c level, i.e., with SO coupling.

a) Puckering of $[\text{Bi}_4]^{4+}$ via D_{4h} symmetric TS

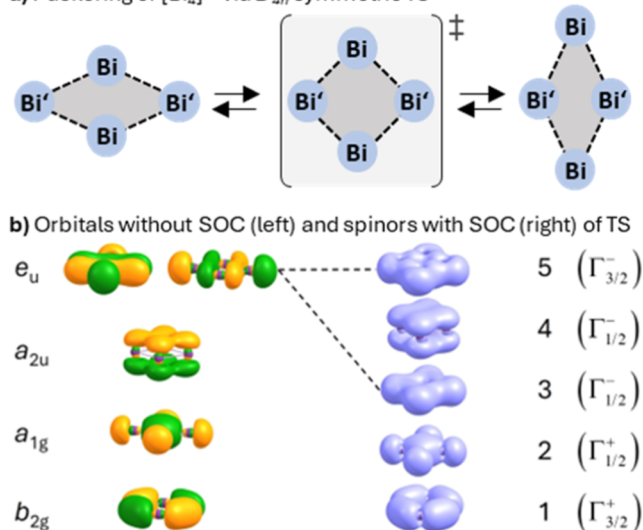


Figure 9. (a) Puckering motion and (b) amplitudes of $\text{Bi}(p)$ MOs from a one-component treatment of $[\text{Bi}_4]^{4+}$, left, and densities of Kramers pairs of spinors from a two-component treatment, right, ordered by their energies.

Bi_4^{4+} (Figure 9b), which hosts the 8 p electrons. Without SOC, the HOMO of the D_{4h} TS is degenerate (e_u), thus half-filled, resulting in a triplet ($b_{2g}^2 a_{1g}^2 a_{2u}^2 e_u^2$). In contrast, the two-

component SOC calculation results in a splitting of the degenerate e_u MO, leading to spinors 3 ($\Gamma_{1/2}^-$) and 5 ($\Gamma_{3/2}^-$), and a singlet occupation $1^2 2^2 3^2 4^2$. Accordingly, only by considering SOC, the puckering can happen on the singlet surface, with a barrier of 29 kJ mol^{-1} for bare $[\text{Bi}_4]^{4+}$.

This also holds for the Bi_4 unit being embedded between the two caps in 1 or 2. A transition structure (optimized at the 2c-ECP/PBE/dhf-TZVP level of theory) with exactly one imaginary frequency of -47.32 cm^{-1} is obtained for 2, featuring a relative energy of 27 kJ mol^{-1} , very similar to bare $[\text{Bi}_4]^{4+}$. This barrier explains the absence of signal splitting for the α -carbon atoms in the ^{13}C NMR spectrum and for the hydrogen atoms in the ^1H NMR spectrum in CD_3CN . It represents, to the best of our knowledge, the first example of fluxionality in an all-metal aromatic ring, and a rare example of structural fluxionality enabled by SOC.³²

Bulk Magnetic Response and the Limits of Diamagnetic Exaltation

To test whether the local diamagnetic response inferred from NMR spectroscopy is reflected also in the bulk magnetic behavior, magnetic measurements were performed on 1 and the reference compound 3. Magnetization data shown in Figure 10 were collected using a SQUID magnetometer equipped with a polypropylene-based airtight sample holder (see ESI, Section 3). All data were obtained after subtracting the SQUID signal of the empty sample holder. The field dependencies imply ferromagnetic impurities, which super-

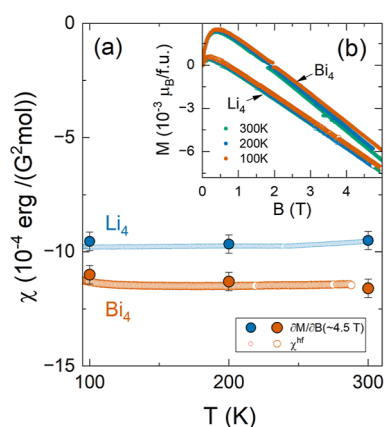


Figure 10. (a) Differential magnetic susceptibility $\partial M/\partial B$ of **1** and **3** at ~ 4.5 T and high-field static magnetic susceptibility χ^{hf} as obtained by the difference of measured magnetization at external magnetic field of $B_2 = 7$ T and $B_1 = 1$ T, respectively, divided by $B_2 - B_1$. χ^{hf} is an experimental approach to dismiss tiny ferromagnetic impurity phases. (b) Isothermal magnetization of **1** and **3** at 100, 200, and 300 K.

impose the diamagnetic response of the main compounds, but do not affect the conclusions regarding the intrinsic diamagnetic response (see ESI, Section 3 for further details). To extract the diamagnetic response of the main phase, we applied three different approaches: (1) calculation of the high-field differential magnetic susceptibility $\partial M/\partial B$ from the measured isothermal magnetization, (2) linear fitting of M vs B data at high fields, and (3) evaluation of the high-field static susceptibility χ^{hf} , which eliminates the response of ferromagnetic impurities.

Both $\chi(T)$ and the isothermal magnetization vary only weakly over the temperature range 100 – 300 K. All three procedures consistently yielded $\chi = -11.3(7) \times 10^{-4}$ erg/(G² mol) for **1** and $\chi = -9.6(5) \times 10^{-4}$ erg/(G² mol) for **3**. The latter is in the order as that estimated from Pascal's constants for **3** ($\chi = -12.4 \times 10^{-4}$ erg/(G² mol)).³³ Taking **3** as the reference, the data suggest an enhanced diamagnetic response of **1** by 18(9)%. However, the significance of this enhancement is limited ($\approx 2\sigma$). More importantly, the experimental value for **1** is lower than the maximum diamagnetic susceptibility predicted from Pascal's constants ($\chi = -17.3 \times 10^{-4}$ erg/(G² mol)), without invoking any additional ring current in the Bi₄ unit. Thus, if the approximate additivity scheme underlying Pascal's constants is taken as a reasonable benchmark, no bulk diamagnetic exaltation is experimentally resolved. Despite clear local NMR signatures of ring-current effects, diamagnetic exaltation therefore does not emerge as a signature of aromaticity in this heavy all-metal system. The availability of actual benchmark compounds (here: **3**) turns out as crucial to assess the presence of bulk diamagnetic exaltation. A plausible reason for the absence of diamagnetic exaltation in our system is the stacked arrangement of the [Bi₄]⁴⁺ ring between two face-to-face calix[4]pyrrolo units, which are themselves diamagnetically responsive. Under an external magnetic field, the diatropic currents induced in the adjacent calix[4]pyrrolo frameworks may modify the local field experienced by the central [Bi₄]⁴⁺ ring and vice versa. Such through-space magnetic interactions could partially offset the simple additivity picture that underlies diamagnetic exaltation arguments and thereby attenuate the net bulk response, even in the presence of a locally significant ring current. While this

interpretation remains tentative and would require further theoretical analysis, it provides a chemically intuitive rationale for why clear local spectroscopic signatures of ring-current behavior are not necessarily mirrored by macroscopic diamagnetic exaltation.

UV/Vis Spectroscopy

Finally, the soluble nature of compound **2** in CH₃CN enabled studies by optical absorption spectroscopy. A solution of **2** (0.43 mM) in CH₃CN was prepared under inert conditions and analyzed at room temperature. The resulting spectrum displays multiple absorption maxima at 716, 460, 364, and 262 nm (Figure 11). The first 500 singlet excitations (up to a

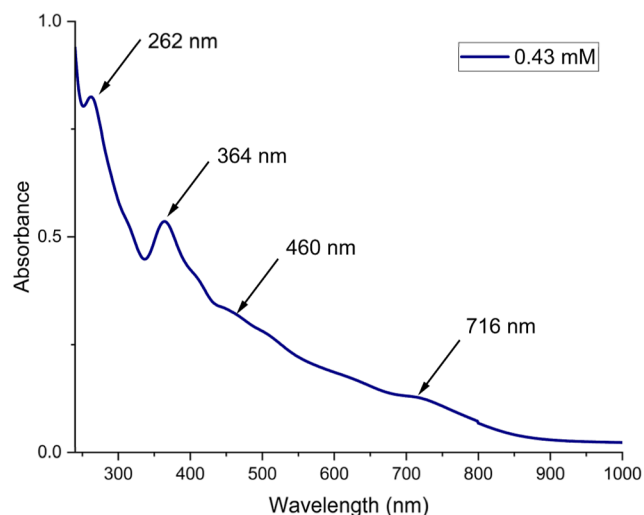


Figure 11. UV–vis spectrum of compound **2** in CH₃CN.

wavelength of 193 nm) were calculated using TDDFT (ECP/PBE0/def2-TZVP (COSMO/CD₃CN)), yielding a good agreement with the measured spectrum (see Figure S49). For the low-lying excitations with wavelengths >500 nm and for the subsequent band of excitations between 400 and 500 nm, difference densities between oscillator-strength weighted excited states and the ground state were calculated (Figure 12).

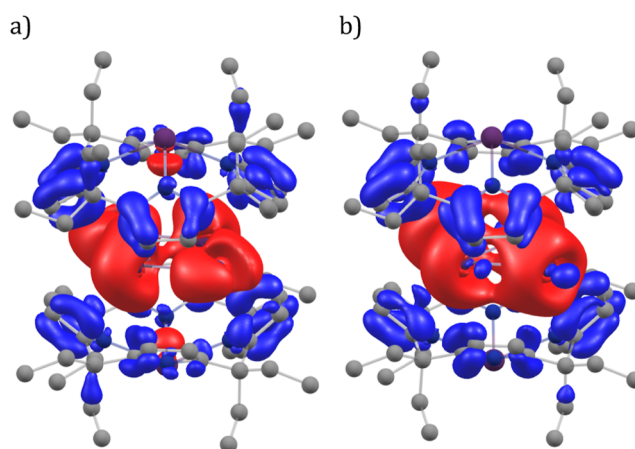


Figure 12. Oscillator-strength-weighted differences of the densities of corresponding ground state and excited states for (a) the range of 400–500 nm and (b) for 500 nm upward. Blue indicates a surplus of electron density in the ground state and red in the excited states. Contours are drawn at ± 0.0005 au.

They reveal that the excitations spectrum is dominated by LMCT transitions from the π -systems of the caps to p-orbitals of the Bi_4 ring. The additional bands at 460 and 364 nm can be assigned to Bi_4 ring-only excitations (computed σ - π^* transitions at 314 and 463 nm, Figure S50).

CONCLUSION

By combining structurally meaningful reference compounds with solid- and solution-state NMR spectroscopy, SQUID magnetometry, mechanistic experiments, and relativistic calculations, we establish direct experimental evidence of magnetically induced ring-current effects in a heavy all-metal system. The pronounced deshielding observed for the Bi_4 -containing compounds is most consistently explained by the magnetic response of the encapsulated rings.

A key advance of this work lies in the comparative framework provided by reference compounds. The isostructural $[\text{Li}_4\text{Br}]^{3+}$ analogue isolates the effect of replacing the central all-metal ring while largely preserving the surrounding supramolecular environment. The binuclear $\text{Bi}(\text{III})$ reference defines the extent to which local heavy atom coordination and ligand-centered perturbation can influence the observed NMR shifts. Together with the close structural similarity across the encapsulated assemblies, this allows global ring current effects to be disentangled from local heavy-atom deshielding, ligand oxidation/dearomatization, and conformational or packing contributions.

The computations reinforce this interpretation on several levels. They support a magnetically responsive, σ -delocalized $[\text{Bi}_4]^{4+}$ core, reproduce the unusual ^1H and ^{13}C NMR shifts of the Bi_4 -containing species, and show that the encapsulated ring retains substantial current-carrying character even in the presence of strong relativistic effects. At the same time, they highlight the importance of spin-orbit coupling not merely for quantitative description, but also for the accessibility of the observed structural dynamics. In this sense, the puckering motion of the rhomboidal $[\text{Bi}_4]^{4+}$ ring represents an unusual example in which fluxional behavior becomes intelligible only within a spin-orbit-coupled picture.

The bulk magnetic measurements define equally important boundary conditions. Despite clear local spectroscopic signatures of ring current behavior, no significant diamagnetic exaltation is resolved for **1**. Thus, in this heavy all-metal system, the bulk susceptibility does not emerge as a reliable proxy for aromaticity. This result calls for caution in the use of macroscopic magnetic criteria for heavy-element clusters, when competing magnetic effects may obscure comparatively subtle manifestations of global delocalization.

We anticipate that supramolecular probes will be broadly useful for experimental studies of the potential aromaticity of metal-only rings, particularly in the heavy element regime, where relativistic effects and local magnetic contributions are inseparable from the chemistry itself.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.6c14973>.

Experimental and computational details including NMR spectra, UV/vis/NIR spectra, and crystallographic data (PDF)

The files 'optimized_structures.txt' contains the cartesian coordinates of all computed structures (TXT)

Accession Codes

Deposition Numbers 2549805–2549808 and 2555562 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via the joint Cambridge Crystallographic Data Centre (CCDC) and Fachinformationszentrum Karlsruhe [Access Structures service](#).

AUTHOR INFORMATION

Corresponding Authors

Florian Weigend – Institute for Quantum Materials and Technologies, Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen 76344, Germany; Email: florian.weigend@kit.edu

Lutz Greb – Anorganisch-Chemisches Institut, Universität Heidelberg, Heidelberg 69120, Germany; orcid.org/0000-0002-5253-419X; Email: greb@uni-heidelberg.de

Authors

Avijit Maiti – Anorganisch-Chemisches Institut, Universität Heidelberg, Heidelberg 69120, Germany; Present Address: Department of Chemistry, Indian Institute of Technology Bhubaneswar, Odisha 752050, India; orcid.org/0000-0001-8388-3096

Jie Zhang – Anorganisch-Chemisches Institut, Universität Heidelberg, Heidelberg 69120, Germany

Ravi Yadav – Anorganisch-Chemisches Institut, Universität Heidelberg, Heidelberg 69120, Germany; Present Address: Department of Chemistry, Indian Institute of Technology Roorkee, Uttarakhand 247667, India; orcid.org/0000-0003-2375-7607

Matthias Heinrich – Kirchhoff-Institut für Physik, Universität Heidelberg, Heidelberg 69120, Germany

Luca Bischof – Kirchhoff-Institut für Physik, Universität Heidelberg, Heidelberg 69120, Germany

Adrian Ellinger – Institute for Quantum Materials and Technologies, Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen 76344, Germany

Manuel Schmitt – Anorganisch-Chemisches Institut, Universität Heidelberg, Heidelberg 69120, Germany; orcid.org/0000-0003-1670-4099

Rüdiger Klingeler – Kirchhoff-Institut für Physik, Universität Heidelberg, Heidelberg 69120, Germany

Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/jacs.6c14973>

Author Contributions

The manuscript was written through the contributions of all authors. All authors have given their approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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