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# Structural insight into halide-coordinated $[\text{Fe}_4\text{S}_4\text{X}_n\text{Y}_{4-n}]^{2-}$ clusters ( $\text{X}, \text{Y} = \text{Cl}, \text{Br}, \text{I}$ ) by XRD and Mössbauer spectroscopy†

Andreas O. Schüren,<sup>a,b</sup> Benjamin M. Ridgway,<sup>b</sup> Florencia Di Salvo,<sup>b,c</sup> Luca M. Carella,<sup>d</sup> Verena K. Gramm,<sup>a</sup> Elisa Metzger,<sup>e</sup> Fabio Doctorovich,<sup>b,c</sup> Eva Rentschler,<sup>d</sup> Volker Schünemann,<sup>e</sup> Uwe Ruschewitz<sup>a</sup> and Axel Klein<sup>a\*</sup>

Iron sulphur halide clusters  $[\text{Fe}_4\text{S}_4\text{Br}_4]^{2-}$  and  $[\text{Fe}_4\text{S}_4\text{X}_2\text{Y}_2]^{2-}$  ( $\text{X}, \text{Y} = \text{Cl}, \text{Br}, \text{I}$ ) were obtained in excellent yields (77 to 78%) and purity from  $[\text{Fe}(\text{CO})_5]$ , elemental sulphur,  $\text{I}_2$  and benzyltrimethylammonium (BTMA<sup>+</sup>) iodide, bromide and chloride. Single crystals of (BTMA)<sub>2</sub>[Fe<sub>4</sub>S<sub>4</sub>Br<sub>4</sub>] (**1**), (BTMA)<sub>2</sub>[Fe<sub>4</sub>S<sub>4</sub>Br<sub>2</sub>Cl<sub>2</sub>] (**2**), (BTMA)<sub>2</sub>[Fe<sub>4</sub>S<sub>4</sub>Cl<sub>2</sub>I<sub>2</sub>] (**3**), and (BTMA)<sub>2</sub>[Fe<sub>4</sub>S<sub>4</sub>Br<sub>2</sub>I<sub>2</sub>] (**4**) were isostructural to the previously reported (BTMA)<sub>2</sub>[Fe<sub>4</sub>S<sub>4</sub>I<sub>4</sub>] (**5**) (monoclinic, Cc). Instead of the chloride cubane cluster  $[\text{Fe}_4\text{S}_4\text{Cl}_4]^{2-}$ , we found the prismane-shaped cluster (BTMA)<sub>3</sub>[Fe<sub>6</sub>S<sub>6</sub>Cl<sub>6</sub>] (**6**) (P1̄). <sup>57</sup>Fe Mössbauer spectroscopy indicates complete delocalisation with Fe<sup>2.5+</sup> oxidation states for all iron atoms. Magnetic measurements showed small  $\chi_{\text{MT}}$  values at 298 K ranging from 1.12 to 1.54 cm<sup>3</sup> K mol<sup>-1</sup>, indicating the dominant antiferromagnetic exchange interactions. With decreasing temperature, the  $\chi_{\text{MT}}$  values decreased to reach a plateau at around 100 K. From about 20 K, the values drop significantly. Fitting the data in the Heisenberg–Dirac–van Vleck (HDVV) as well as the Heisenberg Double Exchange (HDE) formalism confirmed the delocalisation and antiferromagnetic coupling assumed from Mössbauer spectroscopy.

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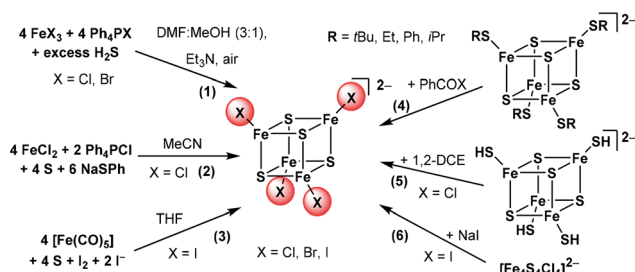
## Introduction

Cubane-shaped  $[\text{Fe}_4\text{S}_4]$  clusters represent a very interesting class of cofactors in biology and are involved in various functions in a cell's life cycle.<sup>1–10</sup> Due to their mixed valence character with formally two ferric (Fe<sup>3+</sup>) and two ferrous (Fe<sup>2+</sup>) iron atoms,  $[\text{Fe}_4\text{S}_4]^{2+}$  clusters show extraordinary electrochemical properties which are crucial for their biological functions in electron transfer and redox catalysis reactions.<sup>1–10</sup> During the last 40 years, numerous  $[\text{Fe}_4\text{S}_4]^{2+}$  clusters with terminal thiolate ligands

have been prepared in order to model the structural, electronic and electrochemical properties as well as the reactivity of the naturally occurring clusters.<sup>5–26</sup> Moreover, the fascinating nature of  $[\text{Fe}_4\text{S}_4]$  clusters has triggered their use as precursors for electrocatalytic materials.<sup>27–33</sup> Halide-based  $[\text{Fe}_4\text{S}_4\text{X}_4]^{2-}$  with  $\text{X} = \text{Cl}, \text{Br}, \text{I}$  are known to be useful precursors because halides can be easily exchanged with thiolate or other ligands by salt metathesis reactions. Homoleptic halide clusters have thus been studied previously and a couple of preparation methods have been published (Scheme 1).<sup>12,14,15,32–48</sup>

<sup>a</sup>Universität zu Köln, Mathematisch-Naturwissenschaftliche Fakultät, Department für Chemie, Institut für Anorganische Chemie, Greinstraße 6, D-50939 Köln, Germany.

E-mail: axel.klein@uni-koeln.de; Tel: +49-221-470-4006

<sup>b</sup>INQUIMAE-CONICET-Universidad de Buenos Aires, Intendente Güiraldes 2160, Pabellón 2, Piso 3, C1428EGA, Buenos Aires, Argentina<sup>c</sup>Universidad de Buenos Aires, Facultad de Ciencias Exactas y Naturales, Departamento de Química Inorgánica, Analítica y Química Física, Intendente Güiraldes 2160, Pabellón 2, Piso 3, C1428EGA, Buenos Aires, Argentina<sup>d</sup>Johannes Gutenberg Universität Mainz, Department Chemie, Duesbergweg 10-14, 55128 Mainz, Germany<sup>e</sup>TU Kaiserslautern Department of Physics, 67663 Kaiserslautern, Germany† Electronic supplementary information (ESI) available. CCDC 2048374, 2048953, 2055695, 2048377, 2048376, 2048378, 2048375 and 2048954. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d2dt03203a>

**Scheme 1** Reported preparation pathways for the  $[\text{Fe}_4\text{S}_4\text{X}_4]^{2-}$  clusters. (1) Müller *et al.*,<sup>37</sup> (2) Kanatzidis *et al.*,<sup>32</sup> (3) Pohl *et al.*,<sup>38–40</sup> (4) Holm *et al.*,<sup>36,41</sup> Henderson *et al.* for  $\text{X} = \text{Cl}$ ,<sup>43–45</sup> Tuzcek *et al.* for  $\text{X} = \text{Cl}$  or  $\text{Br}$ ,<sup>46</sup> (5) Holm *et al.* for  $\text{X} = \text{Cl}$ ,<sup>41</sup> and (6) Holm *et al.* for  $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ,<sup>36</sup> Tuzcek *et al.* for  $\text{X} = \text{I}$ .<sup>46</sup>



We have recently contributed to this very versatile method (3) starting from  $[\text{Fe}(\text{CO})_5]$  and  $(\text{BTMA})\text{X}$  ( $\text{BTMA}$  = benzyltrimethylammonium),  $(\text{Ph}_4\text{P})\text{X}$ , and halogens or interhalogens obtaining excellent yields for the compounds  $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{I}_4]$  and  $(\text{Ph}_4\text{P})_2[\text{Fe}_4\text{S}_4\text{Br}_4]$  containing the homoleptic  $[\text{Fe}_4\text{S}_4\text{X}_4]^{2-}$  clusters.<sup>48</sup> By the same method, we obtained the mixed-halide cluster compounds  $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{BrI}_3]$ ,  $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{ClI}_3]$ , and  $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Cl}_2\text{I}_2]$ . Using  $[\text{Fe}(\text{CO})_5]$ , sulphur, ferrous halides  $\text{FeX}_2$  and  $(\text{BTMA})\text{X}$  and adopting method (2), we obtained  $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Cl}_4]$ ,  $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Br}_4]$ ,  $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Cl}_2\text{I}_2]$ ,  $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Br}_2\text{Cl}_2]$  and  $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Br}_2\text{I}_2]$ . By replacing the halide  $\text{FeX}_2$  with tetrahalido ferrates  $(\text{Ph}_4\text{P})[\text{FeX}_4]$  or  $(\text{Et}_4\text{P})[\text{FeX}_4]$ , we obtained  $(\text{Et}_4\text{N})_2[\text{Fe}_4\text{S}_4\text{Cl}_4]$  and  $(\text{Ph}_4\text{P})_2[\text{Fe}_4\text{S}_4\text{Br}_4]$ . The compounds were obtained in the pure form as microcrystalline solids, while single crystals were not obtained in this study.<sup>48</sup> A careful study of species in solution by UHR-ESI-MS(–) showed that the mixed halide clusters  $[\text{Fe}_4\text{S}_4\text{X}_2\text{Y}_2]^{2-}$  and  $[\text{Fe}_4\text{S}_4\text{XY}_3]^{2-}$  scramble their halide ligands in a coordinative disproportionation in THF solution, yielding all possible species  $[\text{Fe}_4\text{S}_4\text{X}_{4-n}\text{Y}_n]^{2-}$  ( $\text{X}/\text{Y} = \text{Cl}, \text{Br}, \text{I}$ ). The same was concluded from the UV-vis-NIR absorption spectroscopy results in MeCN solution. Powder X-ray diffraction (PXRD) indicated that the compounds  $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Br}_4]$ ,  $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Br}_2\text{Cl}_2]$ ,  $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Cl}_2\text{I}_2]$  and  $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Br}_2\text{I}_2]$  were isostructural to the previously reported  $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{I}_4]$  (monoclinic,  $Cc$ ).<sup>40</sup>

The lack of precise structural information from single crystal XRD was unfortunate since the crystal structures of the  $[\text{Fe}_4\text{S}_4\text{X}_4]^{2-}$  clusters are quite interesting due to the frequent observation that the symmetry of  $[\text{Fe}_4\text{S}_4\text{L}_4]^{n-}$  clusters strongly depends on the packing in the solid state. Frequently, distortion of the idealised cluster symmetry  $T_d$  towards  $D_{2d}$  was observed (Table 1).<sup>22</sup> For the mixed-halide  $[\text{Fe}_4\text{S}_4\text{X}_2\text{Y}_2]^{2-}$  clusters belonging to the vast group of heteroleptic  $[\text{Fe}_4\text{S}_4\text{L}_2\text{L}'_2]^{m-}$  clusters, the  $T_d \rightarrow C_{2v}$  symmetry reduction is immanent in the molecular symmetry of the cluster as is the  $T_d \rightarrow C_{3v}$  symmetry reduction for  $[\text{Fe}_4\text{S}_4\text{L}_3\text{L}'_1]^{m-}$  clusters. At the same time, the packing in the crystal and thus the size and shape of the counter cation can cause lowering of the cluster symmetry and for all three types even lower symmetry caused by crystal packing was reported (Table 1).<sup>37–61</sup> Importantly, with these changes in cluster symmetry, essential properties such as the redox potentials, spin states, magnetic properties, and ligand exchange kinetics vary markedly.<sup>1,6,8,13,14,20–23,37–40,47,50,56,62–84</sup>

Herein, we report the synthesis and detailed study of the materials  $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Br}_4]$  (1),  $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Br}_2\text{Cl}_2]$  (2),  $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Cl}_2\text{I}_2]$  (3),  $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Br}_2\text{I}_2]$  (4), and  $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{I}_4]$  (5) containing cubane type  $\text{Fe}_4\text{S}_4$  clusters alongside with  $(\text{BTMA})_3[\text{Fe}_6\text{S}_6\text{Cl}_6]$  (6) containing the prismane  $[\text{Fe}_6\text{S}_6\text{Cl}_6]^{3-}$  structure. After preparation in solution, the compounds were isolated as single crystals and we can provide full structural information from single crystal and PXRD analyses.

**Table 1** Selected structural features of  $[\text{Fe}_4\text{S}_4\text{L}_4]^{n-}$ ,  $[\text{Fe}_4\text{S}_4\text{L}_3\text{L}'_1]^{n-}$ , and  $[\text{Fe}_4\text{S}_4\text{L}_2\text{L}'_2]^{n-}$  clusters

| Cation   | Ligand set                          | Crystal system | Space group  | Cluster symmetry <sup>a</sup> | Ref.      |
|--|-------------------------------------|----------------|--------------|-------------------------------|-----------|
| $\text{Et}_4\text{N}^+$  | Cl                                  | Monoclinic     | $P2_1/c$     | $D_{2d}$                      | 36 and 42 |
| $n\text{Pr}_4\text{N}^+$   | Cl                                  | Monoclinic     | $P2_1/n$     | $C_1$                         | 41        |
| $\text{Ph}_4\text{P}^+$  | Cl                                  | Monoclinic     | $C2/c$       | $D_{2d}^b$                    | 37        |
| $n\text{Bu}_3\text{NH}^+$  | Cl                                  | Monoclinic     | $P2_1/n$     | $C_{3v}^b$                    | 70        |
| $[\text{K}_4[\text{FeCl}_4](\text{C}_{12}\text{H}_{24}\text{O}_6)_4]^{2+}$ | Cl                                  | Cubic          | $F23$        | $T_d$                         | 52        |
| $[\text{Fe}(\text{MeCN})_2][\text{P}(\text{OMe})_3]_4]^{2+}$               | Cl                                  | Monoclinic     | $P2_1/c$     | $D_{2d}$                      | 85        |
| $\text{Ph}_4\text{P}^+$  | Br                                  | Monoclinic     | $C2/c$       | $D_{2d}^b$                    | 37        |
| $\text{Et}_4\text{N}^+$  | $\text{Br}^e$                       | Monoclinic     | $P2_1/c$     | $S_4$                         | 87        |
| $[(n\text{Bu}_4\text{N})_2[\text{Fe}(\text{DMF})_6]]^{4+}$                 | Br                                  | Monoclinic     | $P2_1/n$     | $T_d$                         | 86        |
| $\text{Ph}_4\text{P}^+$  | I                                   | Tetragonal     | $I4_1/a$     | $S_4$                         | 40        |
| $\text{BTMA}^{+c}$   | I                                   | Monoclinic     | $Cc$         | $C_1$                         | 40        |
| $n\text{Bu}_4\text{N}^+$   | $\text{I}^e$                        | Monoclinic     | $P2_1/n$     | $C_{3v}$                      | 89        |
| $[(\text{Et}_4\text{N})_6[\text{Fe}_2\text{S}_2\text{I}_4]]^{4+}$          | I                                   | Tetragonal     | $P4_2bc$     | $T_d$                         | 60        |
| $n\text{Bu}_4\text{N}^+$   | SMe                                 | Orthorhombic   | $Pba2$       | $T_d$                         | 83        |
| $\text{H}n\text{Bu}_3\text{N}^+$   | SPh                                 | Triclinic      | $P\bar{1}$   | $C_{2v}$                      | 70        |
| $\text{HEt}_3\text{N}^+$   | SPh                                 | Monoclinic     | $P2_1/n$     | $D_{2d}$                      | 70        |
| $\text{BTMA}^{+c}$   | $\text{S}t\text{Bu}$                | Monoclinic     | $P2_1/c$     | $C_1$                         | 82        |
| $\text{Et}_4\text{N}^+$  | $\text{S}t\text{Bu}$                | Tetragonal     | $I\bar{4}2m$ | $D_{2d}$                      | 82        |
| $\text{Ph}_4\text{P}^+$  | 2 Br 2 Cl                           | Monoclinic     | $C2/c$       | $D_{2d}$                      | 37        |
| $\text{Ph}_4\text{P}^+$  | 2 Cl 2 SPh                          | Orthorhombic   | $Pbcn$       | $D_{2d}$                      | 88        |
| $\text{Ph}_4\text{P}^+$  | 2 Cl 2 OPh                          | Orthorhombic   | $Pbcn$       | $D_{2d}$                      | 89        |
| $\text{Ph}_4\text{P}^+$  | 2 SPh 2 $\text{O}p\text{Tol}$       | Orthorhombic   | $P2_12_12_1$ | $C_1$                         | 89        |
| $\text{Ph}_4\text{P}^+$  | 2 Cl 2 S $\text{Et}_2\text{Dtc}^c$  | Monoclinic     | $C2/c$       | $C_2$                         | 91        |
| $\text{Ph}_4\text{P}^+$  | 2 SPh 2 S $\text{Et}_2\text{Dtc}^c$ | Monoclinic     | $C2/c$       | $C_2$                         | 91        |
| $\text{Ph}_4\text{P}^+$  | 3 Cl 1 S $\text{Et}_2\text{Dtc}^c$  | Monoclinic     | $P2_1/c$     | $C_s$                         | 91        |
| $[\text{FeIL}_3]^+$  | 3 I 1 S $\text{Me}_2\text{Tu}^f$    | Triclinic      | $P\bar{1}$   | $C_{3v}$                      | 90        |
| None   | 2 I 2 S $t\text{Bu}_2\text{Tu}^g$   | Monoclinic     | $P2_1/n$     | $C_{2v}$                      | 90        |
| None   | 2 SR 2 S $\text{Et}_2\text{Tu}^h$   | Triclinic      | $P\bar{1}$   | $D_{2d}$                      | 57        |

<sup>a</sup> Approximate symmetry of the cluster. <sup>b</sup> Approaches  $C_{3v}$  symmetry as one Cl ligand shows strong H bonding to  $n\text{Bu}_3\text{NH}^+$ . <sup>c</sup>  $\text{BTMA}^+$  = benzyltrimethylammonium. <sup>d</sup>  $\text{Et}_2\text{Dtc}^- = N,N$ -diethylthiocarbamate. <sup>e</sup> Selenium clusters  $[\text{Fe}_4\text{Se}_4\text{X}_4]^{2-}$ . <sup>f</sup>  $\text{Me}_2\text{Tu} = N,N$ -dimethylthiourea. <sup>g</sup>  $t\text{Bu}_2\text{Tu} = N,N$ -di-*tert*-butyl-thiourea. <sup>h</sup>  $\text{R} = 2,4,6$ -(*i*Pr)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>,  $\text{Et}_2\text{Tu} = N,N$ -diethylthiourea.



Additionally, resonance Raman,  $^{57}\text{Fe}$  Mössbauer and magnetic data were recorded for the first time on such mixed-halide clusters, with the exception of  $(\text{Ph}_4\text{P})_2[\text{Fe}_4\text{S}_4\text{Br}_2\text{Cl}_2]$  for which the structure and Mössbauer data have previously been reported.<sup>37</sup>

## Results and discussion

### Preparations

The materials were prepared as recently described (for details and analyses, see the ESI†). As in our previous study,<sup>48</sup> UHR-ESI-MS(−) showed that the mixed halide clusters  $[\text{Fe}_4\text{S}_4\text{X}_2\text{Y}_2]^{2-}$  scramble their halide ligands leading to coordinative disproportionation in solution yielding all possible species  $[\text{Fe}_4\text{S}_4\text{X}_{4-n}\text{Y}_n]^{2-}$  ( $\text{X}/\text{Y} = \text{Cl}, \text{Br}, \text{and I}$ ) (see the Experimental data in the ESI†). The elemental analyses of the crystallised products clearly show a 2:2 ratio for X:Y. Of course this does not rule out contributions from the 3:1 and 1:3 cluster species, but then both must contribute with the same amount. The same is true for the 4:0 and 0:4 species. Using methods such as resonance Raman, single crystal XRD, PXRD, magnetic measurements and Mössbauer spectroscopy we not only tried to study the local cluster symmetry but also tried to trace other species than the 2:2 complexes  $[\text{Fe}_4\text{S}_4\text{X}_2\text{Y}_2]^{2-}$ .

### Resonance Raman spectroscopy

The resonance Raman spectra of  $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Br}_4]$  (**1**),  $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Br}_2\text{Cl}_2]$  (**2**),  $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Cl}_2\text{I}_2]$  (**3**), and  $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Br}_2\text{I}_2]$  (**4**) were recorded at 458 and 514 nm excitation wavelengths (Fig S1, ESI†). Four bands can be distinguished in the NIR range from 180 to  $580\text{ cm}^{-1}$ . Unfortunately, these bands are quite invariant on the first view which is expectable, as their main contributions come from the Fe–S bridging modes.<sup>46–48,92–94</sup> This is in line with our previous FIR studies and confirms that the absorption bands observed around 500 nm ( $\epsilon$  of about  $2000\text{ cm}^{-1}\text{ M}^{-1}$ ) in the UV-vis-NIR absorption spectra in solution have their origin essentially in the  $\text{Fe}_4\text{S}_4$  cubane ( $\text{S} \rightarrow \text{Fe}$  LMCT).<sup>48</sup> Unfortunately, direct irradiation of the  $\text{X} \rightarrow \text{Fe}$  LMCT band at around 700 nm ( $\epsilon \sim 1500\text{ cm}^{-1}\text{ M}^{-1}$ ) was technically not feasible. Nevertheless, two trends were observed. The introduction of the light  $\text{Cl}^-$  led to a slight high-energy shift of all bands and decreased symmetry led to detectable wavelength dependence for all four bands. In homoleptic compound **1**, only the bands at about 500 and  $400\text{ cm}^{-1}$  vary with the excitation wavelength, while the bands at 283 and  $219\text{ cm}^{-1}$  are completely invariant. The bands which were most sensitive to variation in the halides and wavelength were ranging from 285 to  $276\text{ cm}^{-1}$  and were assigned to the  $T^b_1$  mode in  $T_d$  symmetry while the resonances from 404 to  $398\text{ cm}^{-1}$  probably fit to  $T^b_2$  mode in  $T_d$  symmetry.<sup>46,47,93,94</sup> These modes indicate already a distortion below  $D_{2d}$ .<sup>46</sup> The intense bands at 220 to  $216\text{ cm}^{-1}$  have clearly their origin in the symmetry reduction lower than  $D_{2d}$  for the homoleptic cluster in **1** or lower than  $C_{2v}$  for the heteroleptic derivatives **2**, **3**, and **4**.

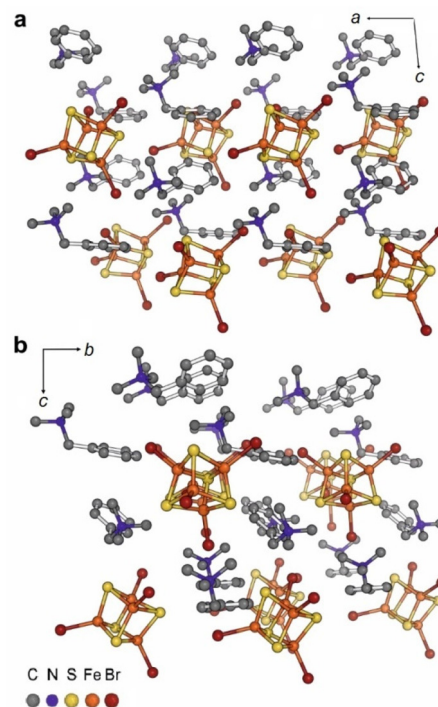
### X-ray crystal structures

Single crystals of high quality were obtained for **1** to **4** and  $(\text{BTMA})_3[\text{Fe}_6\text{S}_6\text{Cl}_6]$  (**6**) directly from the synthesis procedure or were obtained through the slow diffusion of diethyl ether into saturated MeCN solutions. The crystal structures of **1** to **4** were solved and refined in the monoclinic space group  $Cc$ , while that of **5** was found to crystallise in the triclinic space group  $P\bar{1}$  (details in Fig. S2 to S6 and Tables S1–S9 in the ESI†). The  $\text{Fe}_4\text{S}_4$  compounds are thus isostructural to  $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{I}_4]$  (**5**),<sup>40</sup> regardless if they are pure clusters like **1** or mixed halide species like **2**, **3**, and **4**.

Like in  $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{I}_4]$  (**5**),<sup>40</sup> the iron sulphur clusters in  $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Br}_4]$  (**1**) are arranged in planes at the  $[110]$  direction packed with the  $\text{BTMA}^+$  cation in between. The planes are rotated by  $90^\circ$  around the  $c$  axis direction (Fig. 1).

The intermolecular C–H...S and C–H...Br hydrogen bonds with the  $\text{CH}_3$  and  $\text{CH}_2$  groups of the  $\text{BTMA}^+$  cations (Fig. 2) exceed  $3\text{ \AA}$  than the H...X distance and are thus weak.<sup>95</sup> Br...Br interactions between the cluster ions form a chain-like infinite motif along the  $[110]$  direction (Fig. 1 and 2) occurring between Br3 and Br4 are  $3.814(2)\text{ \AA}$  long and thus slightly exceed the sum of the van der Waals radii.<sup>96,97</sup>

The idealised  $T_d$  symmetry of the cubane-shaped  $[\text{Fe}_4\text{S}_4\text{Br}_4]^{2-}$  dianion is significantly decreased. The  $\text{Fe}_4$  cluster core is compressed along the Fe3...Fe4 edge with an extraordinarily short distance of  $2.717(2)\text{ \AA}$  (Tables S2, S5 and S6†). This is  $0.048\text{ \AA}$  shorter than the average of the other Fe...Fe dis-



**Fig. 1** Crystal structure of  $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Br}_4]$  (**1**) viewed along the  $[110]$  direction (a) and rotated by  $90^\circ$  around the crystallographic  $c$  axis to show segregated columns of anions and cations (b). The bottom inset shows atom colouring: H atoms are omitted for clarity.



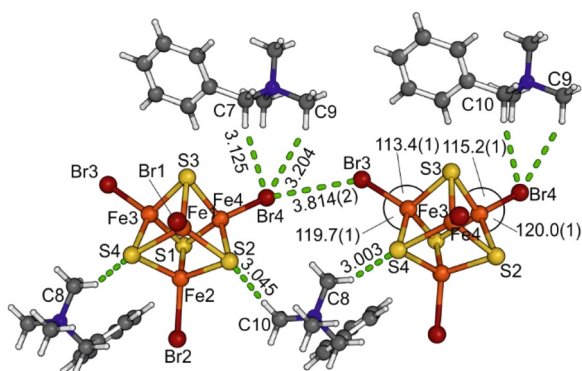


Fig. 2 Intermolecular C–H...S, C–H...Br, and Br...Br interactions in (BTMA)<sub>2</sub>[Fe<sub>4</sub>S<sub>4</sub>Br<sub>4</sub>] (1); distances are in Å and angles are in °.

tances (2.765 Å). The Fe–S bond lengths vary from 2.249(2) to 2.305(2) Å showing four markedly decreased values, one for each Fe atom (Table S2<sup>†</sup>). The analysis of the Br–Fe–Fe and S–Fe–Br angles revealing the asymmetrical distortion of the clusters is connected to the intermolecular Br...Br interactions between Br3 and Br4 (Fig. 2). The Br3–Fe3–Fe4 (138.53(10)°) and the Br4–Fe4–Fe3 (138.03(10)°) angles are smaller than all other Br–Fe–Fe angles (between 140.06(10)° and 151.03(10)°), whereas the opposite S4–Fe3–Br3 (119.66(12)°) and S2–Fe4–Br4 (120.03(12)°) angles are larger compared with 108.30(11) to 118.87(12)°.

The lengths of the other two terminal Fe–Br bonds are not affected by the compression and the values between 2.332(2) and 2.354(2) Å coincide with those observed for the Ph<sub>4</sub>P<sup>+</sup> structure.<sup>37</sup> We thus suspect that the Br...Br interactions are rather repulsive in the packing. In contrast to this, the I...I interactions in (BTMA)<sub>2</sub>[Fe<sub>4</sub>S<sub>4</sub>I<sub>4</sub>] (5) seem to be favorable as the I...I distance of 3.917 Å is below the sum of the van der Waals radii (4.3 Å).<sup>40</sup> In contrast to this, in the PPh<sub>4</sub><sup>+</sup> derivative, the I...I distances are longer which contradicts the idea that the I...I interactions might govern the cluster distortion.<sup>40</sup>

For the mixed-cluster compounds, crystalline material was obtained from (BTMA)<sub>2</sub>[Fe<sub>4</sub>S<sub>4</sub>Br<sub>2</sub>Cl<sub>2</sub>] (2), (BTMA)<sub>2</sub>[Fe<sub>4</sub>S<sub>4</sub>Cl<sub>2</sub>I<sub>2</sub>] (3), and (BTMA)<sub>2</sub>[Fe<sub>4</sub>S<sub>4</sub>Br<sub>2</sub>I<sub>2</sub>] (4) and single crystal XRD data were collected at 293 K and 173 K. All three compounds crystallise isostructural (*Cc*) to the homoleptic 1 and 5<sup>40</sup> and no phase transition was observed on going from 293 to 173 K. The heteroleptic clusters [Fe<sub>4</sub>S<sub>4</sub>X<sub>2</sub>Y<sub>2</sub>]<sup>2-</sup> show mixed occupancies of both halides on each position as reported before for (Ph<sub>4</sub>P)<sub>2</sub>[Fe<sub>4</sub>S<sub>4</sub>Br<sub>2</sub>Cl<sub>2</sub>],<sup>37</sup> and we refined the data of the compounds 2, 3, and 4 using the SUMP command (details and data in the ESI<sup>†</sup>).

In our previous study, we found that in solution and therefore also during synthesis, all possible cubane species [Fe<sub>4</sub>S<sub>4</sub>X<sub>4-x</sub>Y<sub>x</sub>]<sup>2-</sup> (*x* = 0 to 4) are present with [Fe<sub>4</sub>S<sub>4</sub>X<sub>2</sub>Y<sub>2</sub>]<sup>2-</sup> as the dominating one.<sup>48</sup> Since the here reported materials were obtained through slow crystallisation by ether diffusion at -18 °C in the presence of BTMA<sup>+</sup> cations, slight deviations of *x* from the ideal value of 2 in mixed halide clusters [Fe<sub>4</sub>S<sub>4</sub>X<sub>x</sub>Y<sub>4-x</sub>]<sup>2-</sup> might be expected.<sup>37</sup> But only when we were freely refining the

data recorded at 173 K for compound 3 (Cl:I), we obtained a halide ratio of 1.76:2.24 deviating from the ideal 2:2 (Table S10<sup>†</sup>). Unfortunately, the quality of the data did not allow satisfying refinement. The same problems were reported for the structure solution and refinement of (Ph<sub>4</sub>P)<sub>2</sub>[Fe<sub>4</sub>S<sub>4</sub>Br<sub>2</sub>Cl<sub>2</sub>].<sup>37</sup>

In line with earlier assumptions, we believe that the cluster composition and thus the cluster symmetry have no effect on the packing and the clusters arrange randomly in the structures.

A comparison of the unit cell volumes of the mixed-ligand compounds (BTMA)<sub>2</sub>[Fe<sub>4</sub>S<sub>4</sub>X<sub>2</sub>Y<sub>2</sub>] (2 to 4) with those of the homoleptic derivatives 1 and 5 and the calculated cluster volumes using the so-called Solvent Excluded Volume,<sup>98</sup> including the Cl<sub>4</sub> cluster derivative (Fig. 3 and Table 2), showed that by exchanging smaller halides with larger ones, the cell volumes and the cluster volumes increase along the series Cl<sub>4</sub> < Cl<sub>2</sub>Br<sub>2</sub> < Br<sub>4</sub> < Cl<sub>2</sub>I<sub>2</sub> < Br<sub>2</sub>I<sub>2</sub> < I<sub>4</sub> in line with the increasing ionic radii<sup>99</sup> (Cl<sup>-</sup>: 1.81 Å, Br<sup>-</sup>: 1.96 Å, I<sup>-</sup>: 2.20 Å).

This underlines that potential contributions from cluster species with 1:3 and 3:1 ratios cannot be detected if they are present in equal amounts or make only minor contributions. So, we cannot exclude mixed-clusters with 3:1 and 1:3 halide ratios to contribute to the mixed-halide cluster compounds, but we have also no evidence for them.

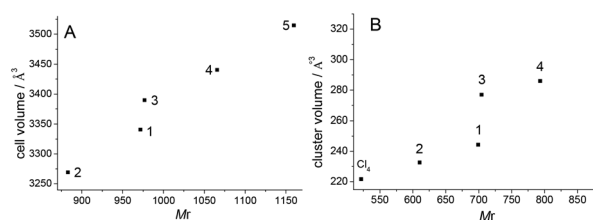


Fig. 3 Comparison of unit cell and the calculated cluster volumes (A) of [Fe<sub>4</sub>S<sub>4</sub>X<sub>4-x</sub>Y<sub>x</sub>]<sup>2-</sup> (*x* = 0 or 2). The calculated so-called solvent excluded volumes (*V*<sub>SE</sub>) (B).<sup>98</sup> Note that the values for 1 to 4 are from data at 173 K, while 5 and "Cl<sub>4</sub>" are from 298 K data.

Table 2 Cell volumes and calculated cluster volumes of [Fe<sub>4</sub>S<sub>4</sub>X<sub>4-x</sub>Y<sub>x</sub>]<sup>2-</sup> clusters (*x* = 0 or 2)<sup>a</sup>

|                                 | Cell volume<br>298 K <sup>b</sup> | Cell volume<br>173 K <sup>b</sup> | Cluster<br>volume<br>298 K <sup>c</sup> | Cluster<br>volume<br>173 K <sup>c</sup> |
|---------------------------------|-----------------------------------|-----------------------------------|---|---|
| Cl <sub>4</sub>                 | — <sup>d</sup>                    | — <sup>d</sup>                    | 221.71 <sup>e</sup>                     | 221.78 <sup>f</sup>                     |
| Cl <sub>2</sub> Br <sub>2</sub> | 3269.0(2)                         | 3201.6(1)                         | 242.51                                  | 232.65                                  |
| Br <sub>4</sub>                 | 3340.8(4)                         | — <sup>d</sup>                    | 244.35                                  | 244.38 <sup>g</sup>                     |
| Cl <sub>2</sub> I <sub>2</sub>  | 3389.6(1)                         | 3323.3(2)                         | 235.62                                  | 277.02                                  |
| Br <sub>2</sub> I <sub>2</sub>  | 3440.5(2)                         | 3342.6(1)                         | 326.00                                  | 286.03                                  |
| I <sub>4</sub>                  | 3514.8(2) <sup>h</sup>            | — <sup>d</sup>                    | 328.66 <sup>h</sup>                     | 328.94 <sup>i</sup>                     |

<sup>a</sup> Values in Å<sup>3</sup>. <sup>b</sup> From single crystal structures of (BTMA) salts. <sup>c</sup> Calculated solvent excluded volume (*V*<sub>SE</sub>).<sup>98</sup> <sup>d</sup> Data not available for BTMA salts; values for other salts are not comparable. <sup>e</sup> Derived from the (Et<sub>4</sub>N)<sub>2</sub>[Fe<sub>4</sub>S<sub>4</sub>Cl<sub>4</sub>] structure determined at 213 K.<sup>36,42</sup> <sup>f</sup> From ref. 49, at 150 K. <sup>g</sup> BzEt<sub>3</sub>N<sup>+</sup> salt at 150 K, from ref. 100. <sup>h</sup> From ref. 40. <sup>i</sup> BzEt<sub>3</sub>N<sup>+</sup> salt at 173 K, from ref. 101.



Due to this, the Fe–X bond distances of the mixed-halide clusters do not allow a straightforward comparison with literature data from (BTMA)<sub>2</sub>[Fe<sub>4</sub>S<sub>4</sub>I<sub>4</sub>] (5),<sup>40</sup> (Ph<sub>4</sub>P)<sub>2</sub>[Fe<sub>4</sub>S<sub>4</sub>I<sub>4</sub>],<sup>40</sup> (Ph<sub>4</sub>P)<sub>2</sub>[Fe<sub>4</sub>S<sub>4</sub>X<sub>4</sub>] (X = Br, Cl),<sup>37</sup> (Et<sub>4</sub>N)<sub>2</sub>[Fe<sub>4</sub>S<sub>4</sub>Cl<sub>4</sub>],<sup>36,42</sup> (nPr<sub>4</sub>N)<sub>2</sub>[Fe<sub>4</sub>S<sub>4</sub>Cl<sub>4</sub>]<sup>41</sup> (Table S7†).

The Fe<sub>4</sub>S<sub>4</sub> cluster cores in the mixed-halide compounds 2 to 4 showed that the characteristic distortion of the [Fe<sub>4</sub>S<sub>4</sub>] core is lower than the D<sub>2d</sub> symmetry (Fig. S5 and S6†). For all three clusters, a significant shortening of the Fe<sub>3</sub>–Fe<sub>4</sub> distance (Tables S5 and S6†) and distortion of the X<sub>3/4</sub>–Fe<sub>3/4</sub>–Fe<sub>4/3</sub> angles and their opposite S–Fe<sub>3/4</sub>–Br<sub>3/4</sub> angles (Table S2†) were found. As for the homoleptic compound 1, the intermolecular halide–halide interactions (Table S5†) were observed parallel to the compressions of the cluster core along the Fe<sub>3</sub>–Fe<sub>4</sub> axis, while at the same time the Fe<sub>1</sub>–Fe<sub>2</sub> axis is slightly elongated (Tables S5 and S6†). For interactions with iodide contribution (*i.e.* I–I, Br–I and Cl–I), the observed distances are always below the sum of the van der Waal radii pointing to an attractive interaction whereas the Br–Br distances are larger as in the homoleptic 1. Br–Cl and Cl–Cl interactions are not observed.

On the other hand, in [Fe<sub>4</sub>S<sub>4</sub>X<sub>4</sub>]<sup>2–</sup> (X = Br or I) derivatives containing R<sub>4</sub>N<sup>+</sup> and Ph<sub>4</sub>P<sup>+</sup> cations,<sup>9,10,29,30,40,56,69</sup> both Br–Br and I–I interactions are longer than in the BTMA<sup>+</sup> structures by least 0.24 Å (Br) and 0.45 Å (I), respectively (Tables S6 and S7†). The halide–halide distances in the homoleptic compounds 1 and 5<sup>40</sup> are also shorter compared with the published Ph<sub>4</sub>P<sup>+</sup> structures.<sup>37,40</sup> This is also in line with the higher density of the BTMA<sup>+</sup> structures (Tables S5 and S6†). As a consequence of these shorter halide–halide interactions, the BTMA<sup>+</sup> structures show markedly higher Fe–Fe distortions for both the homoleptic and the mixed-halide clusters. When taking the difference between the largest and the smallest Fe–Fe distances, the BTMA<sup>+</sup> structures lie at around 0.05 Å (Table S6†), while the Ph<sub>4</sub>P<sup>+</sup> derivatives show values around 0.02 Å (Table S7†). Within the BTMA<sup>+</sup> structures, the homoleptic Br<sub>4</sub> and I<sub>4</sub> show the largest deviations and both these two homoleptic structures and the three mixed-halide structures were found to have the same distortion pattern: two shortened and four extended Fe–Fe distances with overall very low cluster symmetry and very similar cluster shapes (Fig. S5 and S6†).

Attempts to crystallise [Fe<sub>4</sub>S<sub>4</sub>Cl<sub>4</sub>]<sup>2–</sup> with BTMA<sup>+</sup> by the same method led to the formation of a prismane structure (BTMA)<sub>3</sub>[Fe<sub>6</sub>S<sub>6</sub>Cl<sub>6</sub>] (6) which crystallised in the triclinic P $\bar{1}$  space group. The prismane cluster [Fe<sub>6</sub>S<sub>6</sub>Cl<sub>6</sub>]<sup>3–</sup> is positioned on the inversion centre and is surrounded by three BTMA<sup>+</sup> cations (Fig. S2†). Based on this structural feature, the asymmetric unit is represented by two halves of the clusters and three counter ions which can be combined to get two units of 6 per unit cell (Fig. S3†). Pronounced intermolecular H bonding interactions are absent (Fig. S4†). The prismane structure can be described as two alternating layered [Fe<sub>3</sub>S<sub>3</sub>] rings in a chair conformation. Its D<sub>3d</sub> symmetry is only slightly perturbed. The Fe–Cl and Fe–Fe distances are found to be very similar (Table S9†) and comparable to bromide and chloride

prismanes with Et<sub>4</sub>N<sup>+</sup>.<sup>87–91</sup> The Cl–Fe–S angles ranging from 108.26(4)° to 115.96(5)° are quite close to an ideal tetrahedral angle. The bulk material of 6 is not completely phase pure but does definitely not contain the (BTMA)<sub>2</sub>[Fe<sub>4</sub>S<sub>4</sub>Cl<sub>4</sub>] phase isostructural to (BTMA)<sub>2</sub>[Fe<sub>4</sub>S<sub>4</sub>Br<sub>4</sub>] (1) (see Powder XRD). The [Fe<sub>4</sub>S<sub>4</sub>Cl<sub>4</sub>]<sup>2–</sup> cluster was previously crystallised with a number of cations, such as Et<sub>4</sub>N<sup>+</sup>,<sup>36,42</sup> nPr<sub>4</sub>N<sup>+</sup>,<sup>41</sup> or Ph<sub>4</sub>P<sup>+</sup>.<sup>37</sup> We were unable to detect even traces of (BTMA)<sub>2</sub>[Fe<sub>4</sub>S<sub>4</sub>Cl<sub>4</sub>] (see powder XRD, Mössbauer, or magnetic measurement). At the moment, we have no explanation other than a superior crystallisation of prismane 6.

### Powder XRD studies

In previous investigations,<sup>48</sup> we have already shown that the Fe<sub>4</sub>S<sub>4</sub> cluster compounds (1 to 5) are obtained as homogeneous materials with no signs of phase separation. Very weak additional reflections point to some minor impurities of unknown identity. No significant differences between the crystal structures obtained at 170 K and RT are visible excluding the possible phase transitions upon cooling. The diffraction pattern of the Fe<sub>6</sub>S<sub>6</sub> prismane (Fig. S7†) shows that 6 is only a minority phase in the reaction product. It was speculated that the main product could be the still unknown chloride (BTMA)<sub>2</sub>[Fe<sub>4</sub>S<sub>4</sub>Cl<sub>4</sub>]. The simulated diffraction pattern of (BTMA)<sub>2</sub>[Fe<sub>4</sub>S<sub>4</sub>Br<sub>4</sub>] (1) is provided for comparison. Assuming that 1 and the unknown chloride crystallise in the isotopic crystal structures, the pattern of the chloride should be shifted to higher 2θ values thus completely excluding this assumption. However, it should be noted that the formation of the chloride (BTMA)<sub>2</sub>[Fe<sub>4</sub>S<sub>4</sub>Cl<sub>4</sub>] crystallising in another crystal structure cannot completely be ruled out at this point. In addition, another modification of (BTMA)<sub>3</sub>[Fe<sub>6</sub>S<sub>6</sub>Cl<sub>6</sub>] can possibly make up the majority of the studied material.

### <sup>57</sup>Fe Mössbauer spectroscopy

For (BTMA)<sub>2</sub>[Fe<sub>4</sub>S<sub>4</sub>Br<sub>4</sub>] (1) a symmetric doublet with an isomer shift δ = 0.48 mm s<sup>–1</sup> was recorded (Fig. S8A†). Analysis by fitting using a Lorentzian line shape also reveals a quadrupole splitting ΔE<sub>Q</sub> of 1.77 mm s<sup>–1</sup> and a line width at half maximum Γ of 0.42 mm s<sup>–1</sup> (Table 3).

**Table 3** Mössbauer parameters at 77 K of the complexes obtained from spectra fitting analysis<sup>a</sup>

|                | <i>n</i> | δ           | ΔE <sub>Q</sub> | Γ           | Fe   |
|----------------|----------|-------------|-----------------|-------------|------|
| 1              | 100      | 0.48 ± 0.01 | 1.07 ± 0.02     | 0.42 ± 0.01 | 2.5+ |
| 2              | 100      | 0.48 ± 0.01 | 1.07 ± 0.03     | 0.35 ± 0.01 | 2.5+ |
| 3 <sup>b</sup> | A: 50    | 0.48 ± 0.02 | 1.16 ± 0.02     | 0.37 ± 0.02 | 2.5+ |
|                | B: 50    | 0.46 ± 0.01 | 0.80 ± 0.01     | 0.47 ± 0.02 | 2.5+ |
| 4              | 100      | 0.48 ± 0.01 | 1.05 ± 0.02     | 0.35 ± 0.01 | 2.5+ |
| 5 <sup>c</sup> | 89       | 0.48 ± 0.02 | 1.02 ± 0.02     | 0.35 ± 0.01 | 2.5+ |
| 6              | A: 96    | 0.48 ± 0.02 | 0.88 ± 0.02     | 0.35 ± 0.01 | 2.5+ |

<sup>a</sup> Contribution *n*%, isomer shift δ/mm s<sup>–1</sup>, quadrupole splitting ΔE<sub>Q</sub>/mm s<sup>–1</sup>, line width at half maximum Γ/mm s<sup>–1</sup>. Iron oxidation state Fe. <sup>b</sup> Two species simulated in a 50:50 ratio. <sup>c</sup> Minor species of 11% (see text and Fig. S8†).



An isomer shift of  $0.48 \text{ mm s}^{-1}$  is in keeping with the previously reported  $[\text{Fe}_4\text{S}_4\text{Br}_4]^{2-}$  clusters with different counterions.<sup>86,87</sup> It is also in the range observed for  $[\text{4Fe-4S}]^{2+}$  centres occurring in 4Fe-4S proteins. These clusters exhibit complete delocalisation of one electron in the  $\text{Fe}^{2+}\text{-Fe}^{3+}$  spin pairs. The ferromagnetic double exchange between the iron spins formally leads to  $\text{Fe}^{2.5+}\text{-Fe}^{2.5+}$  pairs with the pair spin  $S_p = 9/2$ .<sup>6</sup> In turn, antiparallel (antiferromagnetic) coupling of the pair spins leads to the clusters' diamagnetic ground state.<sup>6,71,75,102,103</sup> The Mössbauer spectrum of **5** was fitted alongside a singlet signal (11%) which can be assigned to monomeric  $(\text{NET}_4)[\text{FeI}_4]^{89}$  (Fig. S8†). Besides this, the behaviour is the same as for **1**. Correspondingly, all Fe atoms in the homoleptic **1** and **5** (Fig. S8†) have an oxidation state of 2.5+.

For both heteroleptic compounds  $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Br}_2\text{Cl}_2]$  (**2**) and  $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Br}_2\text{I}_2]$  (**4**), symmetric Lorentzian-type doublets with  $\delta$  values of  $0.48 \text{ mm s}^{-1}$  were recorded (Fig. S9†). Thus, the average oxidation state of iron in both mixed-halide clusters is 2.5+ with complete delocalisation.

In contrast,  $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Cl}_2\text{I}_2]$  (**3**) exhibited a slightly asymmetric Mössbauer doublet whose analysis reveals the equal contributions of the two species (Fig. 4).

Species A causes a doublet with  $\delta_1 = 0.48 \text{ mm s}^{-1}$  and  $\Delta E_Q = 1.16 \text{ mm s}^{-1}$ . Species B causes an isomer shift with  $\delta_2 = 0.46 \text{ mm s}^{-1}$  which is within the experimental error identical to that of species B. Thus, **3** also has all irons in the 2.5+ oxidation state (Table 3). The different values of  $\Delta E_Q$  may be a result of the large differences in the EN of Cl and I.

It should be noted that in contrast to the analysis with two "nested" doublets presented above, the Mössbauer spectrum of **3** can alternatively be fitted with two "crossed" doublets (Fig. S11†). This leads to  $\delta_A = 0.54$  and  $\delta_B = 0.37 \text{ mm s}^{-1}$  which may indicate electron localisation. However, high spin  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  sites have significantly different  $\Delta E_Q$  values, and the analysis with two "crossed" doublets shows almost identical  $\Delta E_Q$  values of  $1.0 \text{ mm s}^{-1}$  (Fig. S11†) which contradicts elec-

tron localisation. Therefore, we conclude that indeed **3** has all irons in the 2.5+ state.

Such a situation has also been observed for  $[\text{Fe}_4\text{S}_4\text{X}_2\text{Y}_2]^{2-}$  clusters with monodentate ligands X, Y = Cl, OPh and SPH show  $\delta$  values between  $0.46$  and  $0.50 \text{ mm s}^{-1}$  for both coordination sites.<sup>56</sup>

For  $(\text{Ph}_4\text{P})_2[\text{Fe}_4\text{S}_4\text{Br}_4]$ ,  $\delta = 0.488 \text{ mm s}^{-1}$  and  $\Delta E_Q = 0.662 \text{ mm s}^{-1}$  were reported at 77 K.<sup>37</sup> A crude measurement of the mixed-halide compound  $(\text{Ph}_4\text{P})_2[\text{Fe}_4\text{S}_4\text{Br}_2\text{Cl}_2]$  was reported with a shift of about  $0.00 \text{ mm s}^{-1}$  and significant line-broadening<sup>37</sup> similar to that observed for **3**.

The high similarity of all clusters in the BMTA<sup>+</sup> containing materials in their Mössbauer spectra is in line with the very similar distortion of the clusters from  $T_d$  to very low symmetry (see the XRD section).

For  $(\text{BTMA})_3[\text{Fe}_6\text{S}_6\text{Cl}_6]$  (**6**), an isomer shift of  $0.48 \text{ mm s}^{-1}$  was recorded and the oxidation state of each iron inside the prismane core can be assigned to 2.5+. Like the previous prismane cluster, the core of **6** consists of three  $\text{Fe}^{2+}\text{-Fe}^{3+}$  spin pairs coupling ferromagnetically and resulting in  $\text{Fe}^{2.5}$  on average.<sup>86</sup> The observed  $\Delta E_Q$  of  $0.88 \text{ mm s}^{-1}$  is smaller than those reported for other prismanes,<sup>12,38,85-90,102-108</sup> but overall, the isomer shift and the quadrupole splitting for **6** are very similar to those of the  $(\text{Et}_4\text{N})_3[\text{Fe}_6\text{S}_6\text{Cl}_6]$  prismane with  $\delta = 0.495 \text{ mm s}^{-1}$  and  $\Delta E_Q = 1.085 \text{ mm s}^{-1}$  at 125 K.<sup>86</sup>

For fitting the collected data, a second species with a contribution of 4% was necessary. This second doublet was fitted with  $\delta = 1.40$ ,  $\Delta E_Q = 1.01$ , and  $\Gamma = 0.40 \text{ mm s}^{-1}$  and is due to the  $\text{FeCl}_2$  impurities from the starting material (Fig. S10†). For  $(\text{Ph}_4\text{P})_2[\text{Fe}_4\text{S}_4\text{Cl}_4]$ , a  $\delta$  value of  $0.49 \text{ mm s}^{-1}$  was reported at 77 K with a  $\Delta E_Q$  of  $0.67 \text{ mm s}^{-1}$ .<sup>56,86</sup> Although PXRD showed that the crystal structure of  $(\text{BTMA})_3[\text{Fe}_6\text{S}_6\text{Cl}_6]$  is only the minor phase in the isolated material, the Mössbauer results provide good evidence that the major component of the material contains the  $[\text{Fe}_6\text{S}_6\text{Cl}_6]^{3-}$  prismanes. At the same time, the Mössbauer results do not completely rule out the occurrence of the compound  $(\text{BTMA})_4[\text{Fe}_4\text{S}_4\text{Cl}_4]$  as the reported data for  $(\text{Ph}_4\text{P})_2[\text{Fe}_4\text{S}_4\text{Cl}_4]$  is not very different from our data for **6**.

## Magnetic measurements

The molar magnetic susceptibilities of all four compounds are shown in Fig. 5 as  $\chi_M T$  vs.  $T$  plots. All compounds show quite similar magnetic behaviour (Fig. 4 and Fig. S12-S14, ESI†).

At 298 K, the observed  $\chi_M T$  values are  $1.17 \text{ cm}^3 \text{ K mol}^{-1}$ ,  $1.41 \text{ cm}^3 \text{ K mol}^{-1}$ ,  $1.54 \text{ cm}^3 \text{ K mol}^{-1}$  and  $1.12 \text{ cm}^3 \text{ K mol}^{-1}$  for **1** to **4**, respectively, far below the expected spin-only value of  $14.75 \text{ cm}^3 \text{ K mol}^{-1}$  for four uncoupled spins with  $S_1 = S_2 = 4/2$  (ferrous) and  $S_3 = S_4 = 5/2$  (ferric).

Upon lowering the temperature, a steady decrease in the  $\chi_M T$ -products is observed for all compounds, indicating strong dominant antiferromagnetic interactions between the iron ions. Further cooling below 100 K initially leads to no significant change in the values. However, upon cooling only below 20 K, the  $\chi_M T$  values decrease significantly.

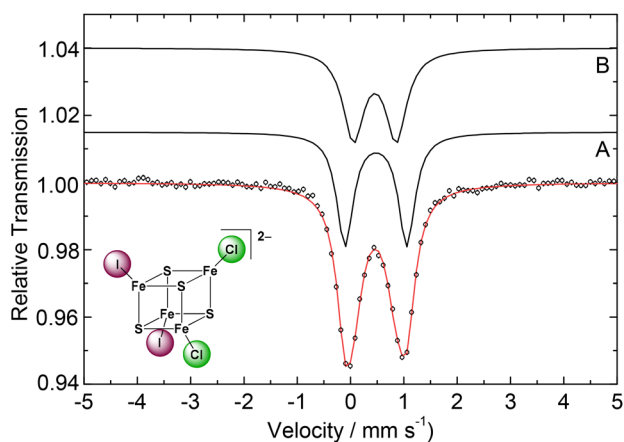
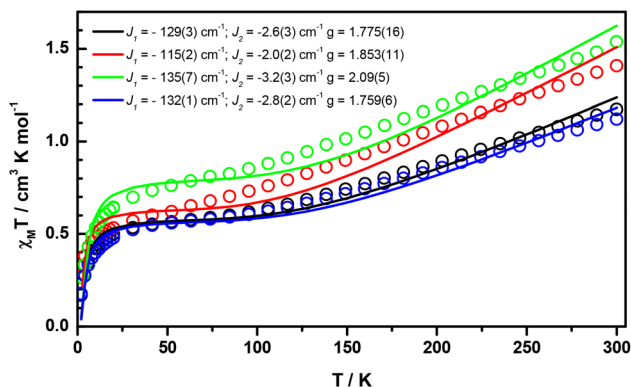


Fig. 4  $^{57}\text{Fe}$  Mössbauer spectrum of  $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Cl}_2\text{I}_2]$  (**3**) at 77 K (dots: collected data, parameters for the simulated species A and B in Table 3).





**Fig. 5** Temperature dependence of the molar magnetic susceptibility depicted as  $\chi_M T$  vs.  $T$  of the homoleptic cluster (BTMA)<sub>2</sub>[Fe<sub>4</sub>S<sub>4</sub>Br<sub>4</sub>] (1, black) and the heteroleptic clusters (BTMA)<sub>2</sub>[Fe<sub>4</sub>S<sub>4</sub>Br<sub>2</sub>Cl<sub>2</sub>] (2, green), (BTMA)<sub>2</sub>[Fe<sub>4</sub>S<sub>4</sub>Cl<sub>2</sub>I<sub>2</sub>] (3, red), and (BTMA)<sub>2</sub>[Fe<sub>4</sub>S<sub>4</sub>Br<sub>2</sub>I<sub>2</sub>] (4, blue).

For cluster systems with four antiferromagnetically coupled spin centres, an HDvV (Heisenberg–Dirac–van Vleck) spin Hamiltonian,  $\hat{H} = -2J_{ij} \sum \hat{S}_i \hat{S}_j$ , with one single exchange interaction parameter  $J$  leads<sup>109</sup> to a highly degenerated spin ground state. However, this assumption is incompatible with the results of the Mössbauer investigations and especially with the observed temperature-dependent magnetic moments for the four compounds (Fig. 5).

The application of a full HDvV with two exchange interactions, which includes a stronger antiferromagnetic exchange interaction  $J_1$ , within the two Fe<sup>2+</sup>–Fe<sup>3+</sup> dimers, and an exchange interaction,  $J_2$ , accounting for the inter-dimer interaction, allows quite satisfactory simulations for the curves for all four compounds (Fig. 5 and Table 4).

However, in three of the four fits, a  $g$  value considerably below 2.0 was obtained. For the Fe<sub>4</sub>S<sub>4</sub> cluster, this phenomenon is well-known<sup>6</sup> and assigned to the presence of spin-dependent delocalisation which is related to the double exchange theory developed by Anderson and Hasegawa.<sup>109</sup> They have shown that resonance delocalisation in a mixed-valence dimer leads to additional splitting  $\pm B(S + 1/2)$  of the energy-split spin ladder  $JS(S + 1)$  for the exchange coupled spin system.

To estimate the double exchange parameter  $B$  in the present Fe<sub>4</sub>S<sub>4</sub> tetramers, we followed the approach recently

reported by Henthorn, Cutsail *et al.*<sup>110</sup> and applied the solved Bleaney–Bowers equation for dimers of high spin d<sup>5</sup>–d<sup>6</sup> mixed-valence centres (Table 4, eqn (S1), (S2), and Fig. S14†). Note that the data at low temperatures were not taken into account for fitting to  $E = -JS(S + 1) \pm B(S + 1/2)$ . This is in accordance with the literature and the interested reader is referred to the publication and the references therein for further information.<sup>110</sup> The values obtained for  $B$  are consistent with the reported values<sup>6,111–113</sup> in all cases and clearly show the presence of electron delocalisation, which is also evident from the Mössbauer data, showing only a single doublet assigned to a mixed valence state. Most importantly, the ratio  $|B/J|$  is relatively small, so the spin ground state of  $S = 1/2$  can be taken as given for the dimers. This justifies the application of the HDvV formalism, which in analogy leads to an  $S = 1/2$  ground state for the antiferromagnetically coupled Fe<sup>2+</sup>–Fe<sup>3+</sup> dimers. Furthermore, with the HDvV-formalism, we are now able to take the inter-dimer interaction into account. Although the values for  $J_2$  are almost two orders of magnitude smaller than  $J_1$ , the resulting final ground states for the Fe<sub>4</sub>S<sub>4</sub><sup>2+</sup>-clusters are diamagnetic with  $S = 0$ , which matches perfectly with the decrease in the  $\chi_M T$  values at low temperature.

In the temperature-dependent magnetisation measurements for (Et<sub>4</sub>N)<sub>2</sub>[Fe<sub>4</sub>S<sub>4</sub>Cl<sub>4</sub>], the magnetic moment  $\mu$  increased from 0.45 to 2.48  $\mu_B$  upon increasing the temperature from 50 to 338 K,<sup>36</sup> which is in good agreement with the behaviour in our compounds.

## Conclusions

The iron sulphur halide clusters [Fe<sub>4</sub>S<sub>4</sub>Br<sub>4</sub>]<sup>2-</sup> and [Fe<sub>4</sub>S<sub>4</sub>X<sub>2</sub>Y<sub>2</sub>]<sup>2-</sup> (X, Y = Cl, Br, I) were synthesised in excellent yields and purity on a gram scale using a recently refined method starting from [Fe(CO)<sub>5</sub>], elemental sulphur, I<sub>2</sub> and benzyltrimethylammonium (BTMA<sup>+</sup>) iodide, bromide and chloride. Through crystallisation, we obtained materials showing a clear 1 : 1 ratio of X : Y for the mixed-halide cluster compounds. Single crystals of (BTMA)<sub>2</sub>[Fe<sub>4</sub>S<sub>4</sub>Br<sub>4</sub>] (1), (BTMA)<sub>2</sub>[Fe<sub>4</sub>S<sub>4</sub>Br<sub>2</sub>Cl<sub>2</sub>] (2), (BTMA)<sub>2</sub>[Fe<sub>4</sub>S<sub>4</sub>Cl<sub>2</sub>I<sub>2</sub>] (3) and (BTMA)<sub>2</sub>[Fe<sub>4</sub>S<sub>4</sub>Br<sub>2</sub>I<sub>2</sub>] (4) were isostructural to the previously reported (BTMA)<sub>2</sub>[Fe<sub>4</sub>S<sub>4</sub>I<sub>4</sub>] (5) (monoclinic,  $Cc$ ). In the same way, we tried to synthesise the previously unknown chloride cubane cluster compound (BTMA)<sub>2</sub>[Fe<sub>4</sub>S<sub>4</sub>Cl<sub>4</sub>]. But we obtained the prismane-shaped cluster (BTMA)<sub>3</sub>[Fe<sub>6</sub>S<sub>6</sub>Cl<sub>6</sub>] (6) ( $P\bar{1}$ ) instead.

No phase transitions were observed for the mixed-halide cluster containing materials from powder XRD at 298 or 170 K or single crystal XRD at 293 and 173 K. Although in solution four different clusters [Fe<sub>4</sub>S<sub>4</sub>X<sub>4-x</sub>Y<sub>x</sub>]<sup>2-</sup> ( $x = 0$  to 4) might occur for the mixed-halide compounds, the structure refinements gave no indication for the X : Y ratio deviating from 2 : 2. Also, a closer look on the cluster volumes (solvent excluded volumes, the unit cell volumes and the cluster distortions) gave evidence for other species than X<sub>2</sub>Y<sub>2</sub>. On the other hand, our XRD data do not rule out X<sub>1</sub>Y<sub>3</sub> species if they were present

**Table 4** Fitting parameter obtained by applying HDvV and HDE<sup>a</sup>

|   | HDvV                 |                      |            | HDE                |                    |          |
|---|----------------------|----------------------|------------|--------------------|--------------------|----------|
|   | $J_1/\text{cm}^{-1}$ | $J_2/\text{cm}^{-1}$ | $g$        | $J/\text{cm}^{-1}$ | $B/\text{cm}^{-1}$ | $g$      |
| 1 | -129 (3)             | -2.6 (3)             | 1.775 (16) | -257 (10)          | 462.2 (5)          | 1.66 (5) |
| 2 | -135 (7)             | -3.2 (3)             | 2.09 (5)   | -256 (10)          | 462.5 (5)          | 1.91 (6) |
| 3 | -115 (2)             | -2.0 (2)             | 1.853 (11) | -274 (13)          | 554.6 (9)          | 1.74 (8) |
| 4 | -132 (1)             | -2.8 (2)             | 1.759 (6)  | -291 (13)          | 552.1 (7)          | 1.65 (6) |

<sup>a</sup> HDvV = Heisenberg–Dirac–van Vleck; HDE = Heisenberg double exchange.



in the same amount as  $X_3Y_1$  species and all cluster species arrange randomly in the structures.

However, Mössbauer spectroscopy rules out larger amounts of such  $X_3Y_1$  species. For the homoleptic **1** and **5** and the mixed-halide clusters **2**, **3**, and **4**, Lorentzian-type doublets were observed in  $^{57}\text{Fe}$  Mössbauer spectroscopy in line with a complete delocalisation with  $\text{Fe}^{2.5+}$  oxidation states for all iron atoms.

Magnetic measurements for **1** to **4** showed small  $\chi_{\text{M}}T$  values at 298 K ranging from 1.12 to 1.54  $\text{cm}^3 \text{K mol}^{-1}$ . From about 20 K, the values drop significantly. Fitting the data in the Heisenberg–Dirac–van Vleck (HDvV) formalism gave  $g$  values markedly below 2 and confirmed the complete delocalisation and antiferromagnetic coupling assumed from Mössbauer spectroscopy.

Thus, the herein described synthesis is reliable and robust and allows the production of mixed-halide clusters  $[\text{Fe}_4\text{S}_4\text{X}_2\text{Y}_2]^{2-}$  ( $X, Y = \text{Cl, Br, I}$ ) on a gram scale and with high purity. In particular, the  $[\text{Fe}_4\text{S}_4\text{Cl}_2\text{I}_2]^{2-}$  derivative might be interesting for further studies as the very different halide ligands might allow the selective substitution of two halide ligands to form new mixed ligand  $[\text{Fe}_4\text{S}_4]$  clusters.

## Experimental section

### Materials

The compounds were prepared and crystallised following already published procedures<sup>48</sup> by diffusion techniques from layered MeCN/diethyl ether mixtures at  $-18^\circ\text{C}$  over a period of 3 weeks. After filtration, washing with diethyl ether and drying under anaerobic and dry atmosphere (argon) using *Schlenck* techniques the opaque black rod shape crystals were stored and prepared for analyses in an argon-filled glove box at room temperature. The details and analytics are available in the ESI.†

### Instrumentation

The resonance Raman spectra were recorded either with 457 nm or 514 nm excitation (13 mW, Coherent Innova 70c) in backscattering geometry using a confocal microscope coupled to a single stage spectrograph (Jobin Yvon XY 800) equipped with a CCD detector.

For  $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Br}_4]$  (**1**),  $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Br}_2\text{Cl}_2]$  (**2**),  $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Br}_2\text{I}_2]$  (**4**) and  $(\text{BTMA})_3[\text{Fe}_6\text{S}_6\text{Cl}_6]$  (**6**), single crystal data collection at 293(2) K was performed using STOE-IPDS (I, II or IIT) diffractometers using graphite-monochromated Mo- $K_\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The samples have been measured in capillaries sealed under an argon atmosphere (0.2 mm diameter). The structures were solved by direct methods using the WinGX<sup>114</sup> package and/or Olex2.<sup>115</sup> For some of them, first structure proposals were obtained with Sir2014.<sup>116</sup> Model refinement was carried out with SHELXL2018/1<sup>117,118</sup> by employing full-matrix least-squares methods on  $F^2$ . All non-hydrogen atoms were treated anisotropic and the hydrogen atoms were included by using appropriate riding models. Numeric absorption correction was performed using X-Red<sup>119</sup> and X-Shape<sup>120</sup> packages. CCDC

Deposition Numbers are 2048374 for  $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Br}_4]$  (**1**), 2048953 for  $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Br}_2\text{Cl}_2]$  (**2**), 2055695 for  $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Br}_2\text{I}_2]$  (**4**), and 2048377 for  $(\text{BTMA})_3[\text{Fe}_6\text{S}_6\text{Cl}_6]$  (**6**), respectively.†

For  $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Br}_2\text{Cl}_2]$  (**2**),  $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Cl}_2\text{I}_2]$  (**3**) and  $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Br}_2\text{I}_2]$  (**4**), LT single crystal data were collected at 173(2) K and for  $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Cl}_2\text{I}_2]$  (**3**) at 293(2) K using an Oxford Diffraction Xcalibur Gemini Eos diffractometer using graphite-monochromated Mo- $K_\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The crystals were transferred under argon to Paratone oil and mounted on a nylon loop. For cooling, cold dry air was provided by an Oxford Cryosystems Desktop Cooler. CrysAlis Pro,<sup>121</sup> from Oxford Diffraction, was used to collect the initial frames for determination of the unit cell. Subsequently, the program was used to plan a data collection. In most cases, a full sphere of data were collected. After collection, data reduction was carried out with the CrysAlis Pro suite and multiscan absorption correction was carried out (SCALE3 ABSPACK scaling algorithm).<sup>122</sup> The space group selection was made using the inbuilt program, GRAL, which selected the monoclinic space group  $Cc$  for all structures. The output files were used for initial structure solution using SHELXL<sup>123</sup> or Olex2.<sup>115</sup> Subsequently, the structures were refined using SHELXL 2018/1.<sup>117,118</sup> The mixed-halide clusters showed signs of disorder and this was modelled at first by allowing the occupancies for the halide ligands to refine freely. In the final refinement, the occupancies of the disordered pairs of halides, *i.e.*, bromide and chloride, iodide and chloride, or bromide and iodide, were restrained using the SUMP command (SHELXL).<sup>117,118</sup> In all cases, this strategy resulted to be more adequate to treat the data and obtain better quality refinement indicators and realistic Fe–X and X...Y distances. The CCDC Deposition Numbers are 2048376, 2048378, 2048375 (173 K) and 2048954 (293 K) for  $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Br}_2\text{Cl}_2]$  (**2**),  $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Cl}_2\text{I}_2]$  (**3**), and  $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Br}_2\text{I}_2]$  (**4**), respectively.†

The selected bond lengths and angles of the compounds were calculated using the PLATON software.<sup>124</sup> The graphical representations were done by Mercury<sup>125</sup> and PyMOL,<sup>126</sup> and the editing of CIF files was performed using the PubCif<sup>127</sup> software.

Synchrotron X-ray powder diffraction data collection was performed at DESY (Hamburg, beamline P02.1, storage ring Petra III with  $\lambda = 0.207203 \text{ \AA}$  and a PerkinElmer XRD 1621 flat panel detector). The samples were measured in capillaries sealed under an argon atmosphere (0.5 mm diameter). The collected data was transformed with Fit2d<sup>128</sup> and analysed with WinXPow.<sup>129</sup>

The  $^{57}\text{Fe}$  Mössbauer data were recorded in the transmission geometry using a constant acceleration spectrometer operated in conjunction with a 512-channel analyser in the time-scale mode (WissEl GmbH) using Wissoft 2003. The detector consisted of a proportional counter and the source contained  $^{57}\text{Co}$  diffused in Rh with an activity of 1.4 GBq. The spectrometer was calibrated against  $\alpha$ -iron at room temperature. Sample cooling to 77 K was achieved by placing the samples in a con-





tinuous flow cryostat from Oxford Instruments. The spectral data were transferred from the multi-channel analyser to a PC for further analysis employing the public domain program Vinda<sup>130</sup> running on the Microsoft Excel 2003® platform. The spectra were analysed by least-squares fits using Lorentzian line shapes.

The magnetic measurements were performed with a Quantum Design MPMS-XL-7 SQUID magnetometer using powdered microcrystalline samples. The variable temperature susceptibility data were collected in the temperature range of 2 to 300 K under an applied field of 0.1 Tesla. The experimental susceptibility data were corrected for the temperature-dependent magnetic contribution of the holder and the underlying diamagnetism using Pascal's constants.

## Author contributions

AOS: investigation, data curation, visualisation, writing – original draft, and funding acquisition. BMR: investigation, data curation, and visualisation. FDS: data curation, visualisation, and supervision. LC: investigation, data curation, validation, and visualisation. VKG: investigation, data curation, and visualisation. FD: methodology, validation, project administration, supervision, and funding acquisition. ERE: methodology, validation, and supervision. VS: methodology, validation, and supervision. UR: methodology, validation, project administration, supervision, funding acquisition, and writing – review and editing. AK: methodology, validation, project administration, supervision, and writing – review and editing.

## Conflicts of interest

There are no conflicts to declare.

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