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Chalcogen bond activation in cation radical salts of naphthalene *peri*-diselenides with $S = 5/2$ magnetic anions

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The activation of strong σ -holes in the oxidized form of 2,7-dimethoxynaphthalene *peri*-diselenide (**1**) is demonstrated in its radical salts with magnetic ($S = 5/2$) FeX_4^- anions as well as their diamagnetic analogs GaX_4^- ($X = \text{Cl}, \text{Br}$). All four salts exhibit short and directional $\text{Se}\cdots\text{X}$ chalcogen bonding (ChB) interactions, together with strong dimerization of the radical species into dicationic dimers along the stacks of $\mathbf{1}^{+\cdot}$. Magnetic analysis highlights the presence of antiferromagnetic interactions between paramagnetic FeX_4^- anions and reveals long-range antiferromagnetic order with $T_N = 5.9$ K only in the FeBr_4^- salt, attributable to the short $\text{Br}\cdots\text{Br}$ distances induced by ChB interactions.

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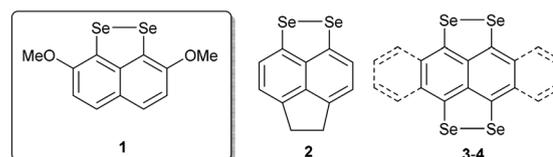
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Introduction

The solid-state chemistry of π -type radicals¹ is based on a combination of (i) intermolecular interactions found in any molecular solid (van der Waals interactions, π - π interactions, hydrogen/halogen/chalcogen bonding)² and (ii) overlap interactions of the SOMO of such open-shell species. The outcome of such combined interactions governs their magnetic properties, encompassing non- or weakly interacting species, strongly dimerized systems, and extended systems exhibiting long-range magnetic correlations.³ Among π -type radicals, cationic species such as those derived from tetrathiafulvalene (TTF) derivatives occupy a special place in this landscape, as (i) they can crystallize into mixed-valence, highly conducting salts,⁴ and (ii) oxidation to the radical cation state activates the TTF substituents, enabling enhanced supramolecular interactions through stronger hydrogen, halogen or chalcogen bonding. This has been revealed recently through substitution of the TTF core with halogens (I, Br),^{5,6} or selenomethyl (SeMe) moieties,⁷ as the oxidation of the TTF strongly reinforces the σ -hole in the prolongation of the $\text{C}_{\text{TTF}}\text{-I}$ or $\text{C}_{\text{TTF}}\text{-Se}$ bond, for interactions with the counter ion (Cl^- , Br^- , ClO_4^- , TCNQF_n^- , ...) acting as Lewis base. One added value to these directional interactions could be the association of such activated TTFs cation radicals ($S = 1/2$) with paramagnetic anions such as the prototypical $S = 5/2$ $\text{Fe}^{\text{III}}\text{Cl}_4^-$. Such systems are indeed expected

to favor so-called π -d interactions between the delocalized π -type conducting electrons of the donor and the localized d-type magnetic anions.^{8,9} The emergence of delicately balanced such π -d interactions can indeed give rise to intriguing spin-charge coupled phenomena, such as giant magnetoresistance and field-induced superconductivity.¹⁰ Along this line, the introduction of halogen bonding have also proven successful in controlling intermolecular interactions between donor and FeX_4^- anions, as illustrated in $(\text{EDO-TTFBr}_2)_2\text{FeX}_4$ ($X = \text{Cl}, \text{Br}$) salts and analogs.^{11,12} However, this attractive approach is hampered by the spin density distribution in iodo- and selenomethyl-substituted TTFs, essentially localized on the central C_2S_4 TTF moiety, with very small spin density on outer halogen/chalcogen substituents.⁷ As a consequence, direct magnetic interactions are very limited. In order to circumvent this issue, we turn our interest to non-TTF-based electron donors where both HOMO and spin density distribution will be concentrated on those atoms prone to simultaneously act as halogen- or chalcogen bond donors. We accordingly considered electron-rich diselenides and tetraselenides such as **1-4**.



Indeed, as shown in Fig. 1 for compound **1** (2,7-dimethoxynaphthalene *peri*-diselenide), the HOMO and spin density are highly concentrated on the selenium atoms. Furthermore, cal-

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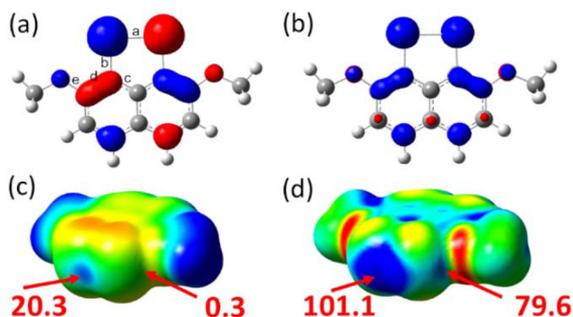


Fig. 1 Electronic properties of **1** with (a) HOMO, (b) spin density distribution in $1^{+\bullet}$, ESP surface of (c) neutral **1**, and (d) ESP surface of radical cation ($1^{+\bullet}$) with $V_{s,max}$ values reported in kcal mol^{-1} .

culated electrostatic potential (ESP) surface of the cation radical $1^{+\bullet}$ shows the presence of σ -holes located in the molecular plane and able to interact with anions through ChB, two in the prolongation of the Se–Se bond, and one perpendicular to this Se–Se bond, corresponding to the merging of the two individual σ -holes in the prolongation of the C–Se bonds. We have already shown that such σ -hole localization is general among cyclic diselenides,^{13,14} and we demonstrate here that their amplitude is strongly enhanced when going from the neutral (Fig. 1c) to the cation radical state (Fig. 1d). Also, we noticed that compounds **3** and **4** in their reported chloride salts,^{15,16} are indeed engaged in short Se...Cl[−] ChB.

In that respect, the diselenide **1** was reported to form only *neutral* charge transfer complexes with TCNQ, without any report on their crystal structures.¹⁷ We demonstrate here that **1** can be successfully oxidized into stable cation radicals, which were isolated in the present work with magnetic ($S = 5/2$) FeX_4^- anions as well as their diamagnetic analogs GaX_4^- ($X = \text{Cl}, \text{Br}$), affording the corresponding 1:1 salts, characterized with strong antiferromagnetic interactions and a long-range antiferromagnetically ordered ground state for the FeBr_4^- salt.

Results and discussion

Donor molecule **1** was prepared as previously described¹⁸ from 1,8-dibromo-2,7-dimethoxynaphthalene, with minor modifications reported in SI. Its oxidation potential was measured at 0.62 V vs. SCE in CH_2Cl_2 (+0.18 V vs. Fc^+/Fc).^{17a} Electrocrystallization experiments were conducted with the $n\text{-Bu}_4\text{N}^+$ salts of FeCl_4^- and FeBr_4^- , and their diamagnetic analogs GaCl_4^- and GaBr_4^- , affording four salts with 1:1 stoichiometry, formulated as $(\mathbf{1})(\text{FeX}_4^-)$ or $(\mathbf{1})(\text{GaX}_4^-)$. As shown in Table S1, the salts with FeCl_4^- , FeBr_4^- and GaBr_4^- are isostructural. They crystallize in the monoclinic system, space group $P2_1/n$ with both $1^{+\bullet}$ cation and anion in general position. The GaCl_4^- crystallizes in the triclinic system, space group $P\bar{1}$, with both $1^{+\bullet}$ cation and anion in general position but with the GaCl_4^- anion disordered on two positions with a 91:9 distribution. The overall solid-state organization of the cation and

the anion in $(\mathbf{1})(\text{GaCl}_4^-)$ is however closely related to that of the three other salts (*vide infra*). Note that a second phase of $(\mathbf{1})(\text{GaCl}_4^-)$, denoted $(\mathbf{1})(\text{GaCl}_4^-)_B$ was identified concomitantly. It crystallizes in the triclinic group $P\bar{1}$, with twice the volume of the former one, two independent $1^{+\bullet}$ cations and two independent, disordered GaCl_4^- anions. It is described in more details in SI (Fig. S3–S6).

We note sizeable evolutions of the intramolecular bond distances in $1^{+\bullet}$, when compared with its neutral counterpart **1** (Table S4). It appears indeed that the bonds a (Se–Se), b (C–Se) and e (C–OMe), of antibonding nature in the HOMO of **1** (*cf.* Fig. 1a in which the bond notation is also given) shorten upon oxidation (−1.4, −1.7 and −2.3% respectively), while bonds d (C–C), of bonding nature in the HOMO, lengthen upon oxidation by +2.4%. The bonds c (C–C) are not modified, consistent with their nonbonding nature in the HOMO as one C atom is located on an orbital node.

A view of the unit cell of $(\mathbf{1})(\text{FeCl}_4^-)$ is shown in Fig. 2 as a representative example of the four salts (see Fig. S7–S9). The salts are characterized by stacks of cation radicals running along the *a* direction. Along the stacks, the molecules adopt two different inversion-centered head-to-tail overlaps (Fig. 2b and c), with very different interplanar distances, found in $(\mathbf{1})(\text{FeCl}_4^-)$ at 3.19 and 3.49 Å, in $(\mathbf{1})(\text{GaCl}_4^-)$ at 3.21 and 3.47 Å, in $(\mathbf{1})(\text{FeBr}_4^-)$ at 3.20 and 3.51 Å, and in $(\mathbf{1})(\text{GaBr}_4^-)$ at 3.21 and 3.51 Å. The intra-dimer plane-to-plane distances (3.19–3.21 Å) are notably shorter than the C...Se van der Waals contact distances (3.60 Å), indicating a strong dimerization of the $S = 1/2$ radical species into dicationic dimers in all salts.

The dimerized chains are surrounded by the Fe/GaX_4^- anions, with short and directional Se...X ($X = \text{Cl}, \text{Br}$) contacts characteristic of ChB interactions. Indeed, as detailed in Fig. 3 for $(\mathbf{1})(\text{FeCl}_4^-)$, two Cl atoms (Cl1 and Cl4) lie in the molecular

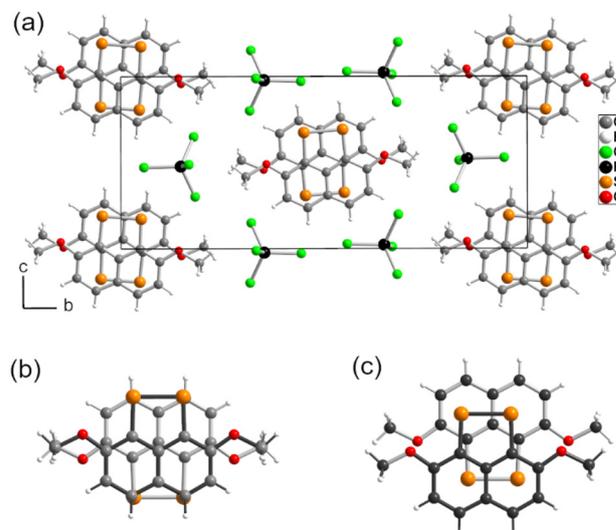


Fig. 2 Structure of $(\mathbf{1})(\text{FeCl}_4^-)$ with: (a) projection view of the unit cell along *a*, (b) intra-dimer overlap pattern with a plane-to-plane distance of 3.19 Å, and (c) inter-dimer overlap pattern with a plane-to-plane distance of 3.49 Å.



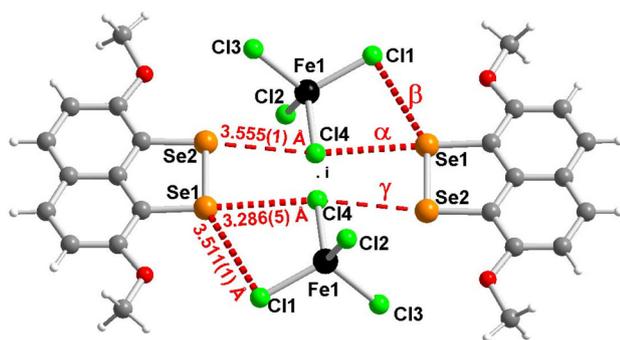


Fig. 3 Detail of the ChB interactions (red dotted lines) in (1)(FeCl₄).

plane of the donor molecule, allowing for the setting of two ChB interactions with Se1, noted α and β in Fig. 3, at 3.286(5) and 3.511(1) Å, corresponding to a reduction ratio (RR) of respectively 0.90 and 0.96. A third ChB interaction (noted γ) with the inversion-related FeCl₄⁻ anion is observed between Se2 and Cl4 (RR = 0.97). This organization pattern is essentially similar in the other salts (see Fig. S10–S12 in SI), with variations associated with the smaller size of GaCl₄⁻, with the larger radius of Br in the FeBr₄⁻ and GaBr₄⁻ anions. ChB distances are collected in Table 1.

Transport measurements performed on single crystals by the two-point method show for all four salts an essentially insulating behavior with σ_{RT} values of 8.1×10^{-7} and 1.9×10^{-8} S cm⁻¹ in the FeCl₄⁻ and FeBr₄⁻ salts respectively, and 2.3×10^{-8} and 8.0×10^{-9} S cm⁻¹ in the GaCl₄⁻ and GaBr₄⁻ salts respectively. These values confirm the very strong dimerization of the 1⁺ radicals within the stacks.

Magnetic susceptibility (χ) measurements performed on a polycrystalline sample of the two GaCl₄⁻ and GaBr₄⁻ salts indicate their diamagnetic behavior. This confirms the analysis made above based on the crystal structures and shows that the $S = 1/2$ 1⁺ radicals are strongly paired into the dimerized chains and do not contribute to the magnetism below 300 K. This result implies that the magnetic response of the two FeCl₄⁻ and FeBr₄⁻ salts is attributable only to the contributions of the inorganic anions.

To probe and compare magnetic behaviors of the two FeCl₄⁻ and FeBr₄⁻ salts, variable-temperature dc magnetic susceptibility data were collected for microcrystalline samples. The resulting plot of χT vs. T is shown in Fig. 4. At 300 K, the χT value is $4.4 \text{ cm}^3 \text{ K mol}^{-1}$ for both compounds, in good agreement with the expected contribution of a high-spin $S = 5/2$ Fe^{III} ion ($C = 4.375 \text{ cm}^3 \text{ K mol}^{-1}$ with $g = 2$; g being the

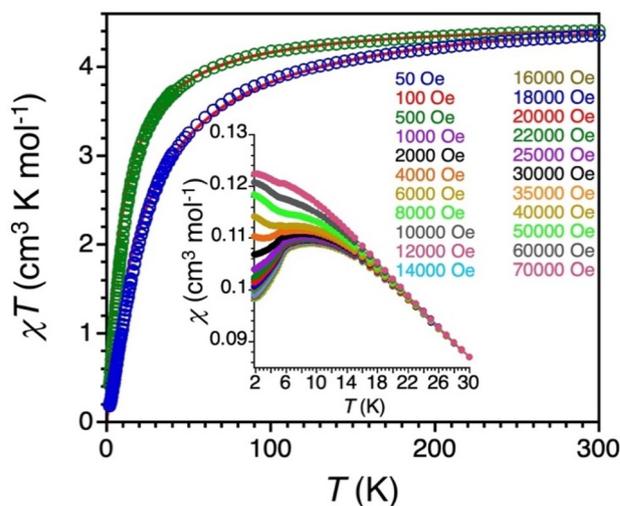


Fig. 4 Temperature dependence of the χT product measured at 0.1 T for the FeCl₄⁻ (in green open circles) and FeBr₄⁻ (in blue open circles) salts (where $\chi = M/H$ is the magnetic susceptibility normalized per mole of formula unit, i.e. per one mole of Fe center). The solid red lines are the best fits of the experimental data between 25 and 300 K to the Curie–Weiss law, leading to $C = 4.54$ and $4.71 \text{ cm}^3 \text{ K mol}^{-1}$ and $\theta = -9.1$ and -23.2 K , for the FeCl₄⁻ and FeBr₄⁻ salts, respectively. Inset: temperature dependence of the molar magnetic susceptibility for a polycrystalline sample of the FeBr₄⁻ salt at different dc fields up to 7 T. Solid lines are guides for the eye.

Landé factor). Upon lowering temperature, the χT product gradually decreases, reaching values of 0.4 and $0.2 \text{ cm}^3 \text{ K mol}^{-1}$ at 1.85 K for the FeCl₄⁻ and FeBr₄⁻ salts, respectively. Such thermal behavior indicates the presence of predominant antiferromagnetic interactions between the Fe^{III} spins. Notably, the χT product of the FeBr₄⁻ salt falls at higher temperature than that of the FeCl₄⁻ salt, suggesting stronger antiferromagnetic interactions in the former.

Indeed, the plot of χ^{-1} vs. T (Fig. S13 in SI) displays a linear relationship in the 30–300 K temperature range, consistent with a Curie–Weiss law ($g = 2.0$ and 2.1 and $\theta = -9.1$ and -23 K for the FeCl₄⁻ and FeBr₄⁻ salts, respectively), thereby confirming the stronger antiferromagnetic interaction in the FeBr₄⁻ salt.

To further investigate the low temperature magnetic behavior, variable-field magnetization data were collected for both compounds below 15 K as shown in Fig. 5. At 1.85 K, the M vs. H data are non-linear for both compounds, reaching 3.8 and $1.6 \mu_B$ at 7 T for the FeCl₄⁻ and FeBr₄⁻ salts, respectively. These values are significantly lower than the expected saturation value of $5 \mu_B$, particularly in the case of the FeBr₄⁻ salt. The deviation from linear field dependence is highlighted by a broad maximum in the dM/dH vs. H plot for the FeCl₄⁻ salt (Fig. S14). This feature is nearly independent of temperature and does not extrapolate to zero at finite temperature, likely indicating the presence of antiferromagnetic interactions between Fe^{III} centers that are compensated by the applied magnetic field at $H^*(0) = 4.25 \text{ T}$ (value extrapolated at zero).

Table 1 Se...X (X = Cl, Br) ChB distances in the four salts

	α ChB (Å), RR	β ChB (Å), RR	γ ChB (Å), RR
(1)(FeCl ₄)	3.286(5), 0.90	3.511(1), 0.96	3.555(1), 0.97
(1)(GaCl ₄)	3.255(11), 0.89	3.503(6), 0.96	3.593(7), 0.98
(1)(FeBr ₄)	3.377(5), 0.90	3.634(1), 0.97	3.750(1), 1.00
(1)(GaBr ₄)	3.413(9), 0.91	3.658(2), 0.97	3.734(1), 0.99



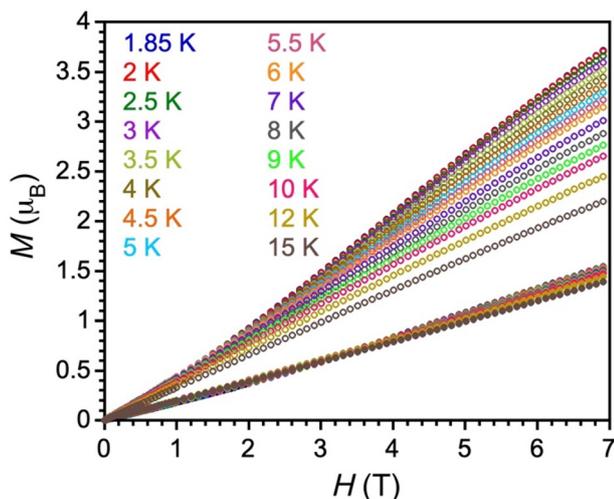


Fig. 5 Field dependence of the magnetization up to 7 T at indicated temperatures between 1.85 and 15 K for the FeCl_4^- (in open circles) and FeBr_4^- (in full circles) salts.

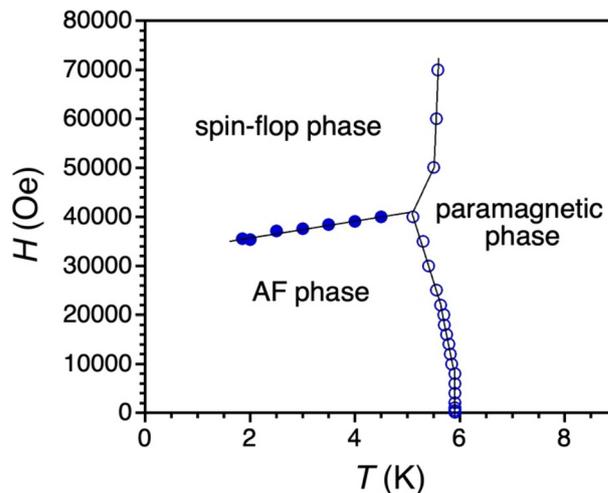


Fig. 6 (T, H) phase diagram for the FeBr_4^- salt. Full circles: location of the maximum of susceptibility from dM/dH vs. H data (Fig. S15); open circles: location of the maximum of susceptibility from χ vs. T data (Fig. 4 inset). The solid lines are guides.

The average magnetic exchange is estimated at $zJ'/k_B = -1.1$ K from the field/interaction energy equality, $g\mu_B SH^*(0) = 2|zJ'|S^2$.¹⁹ It is worth mentioning that, despite the observance of H^* and the field-dependence shown in χ vs. T data (Fig. S15; or non-linearity of the M vs. H data), an ordered antiferromagnetic ground state was not observed in the FeCl_4^- salt above 1.85 K.

In contrast, the dM/dH vs. H plot of the FeBr_4^- salt shows a sharp peak at 1.85 K (Fig. S16). Moreover, χ vs. T data reveal strong field-dependence with a pronounced low-temperature drop at low fields (Fig. 4 inset). By combining M vs. H and χ vs. T data, and taking the maximum of the dM/dH vs. H and χ vs. T plots, the characteristic field, H_C , was tracked to construct a (T, H) phase diagram, shown in Fig. 6. The extrapolation of the characteristic field to zero at a finite temperature confirms the presence of an 3D antiferromagnetic order with $T_N = 5.9$ K. When a magnetic field is applied, a transition line corresponding to H_{C1} emerges, that is only weakly temperature dependent. At higher magnetic fields, $H > H_{C1}$, a quasi-vertical transition line continues around 5.6 K. This observation, together with the gradual magnetization increase under applied dc field, suggests the presence of three different magnetic phases with an antiferromagnetic (AF)-to-spin-flop (SF) phase transition at H_{C1} ,²⁰ resulting from the competition between anisotropy (E_a) and the Zeeman energies.²¹ H_{C2} corresponding to the SF-to-paramagnetic phase transition is not accessible in the experimental window of dc fields. Nevertheless, neglecting anisotropy contribution on H_{C2} ($H_E \gg H_A$, where H_A and H_E are anisotropy and exchange fields, respectively) this field can be estimated from the perpendicular susceptibility, χ_{perp} , obtained experimentally by the slope of the M vs. H data at 1.85 K at $H > H_{C1}$: $H_{C2} \approx Ng\mu_B S/\chi_{\text{perp}} \approx 21$ T.

A quantitative analysis of the effect of the applied field is possible at $T = 0$ K where entropy vanishes, and the

expressions for $H_{C1}(0)$ and $H_{C2}(0)$ are given by the following equations for $g = 2$:²²

$$H_{C1}(0)^2 = 2H_A H_E - H_A^2 \quad (1)$$

$$H_{C2}(0) = 2H_E - H_A \quad (2)$$

By taking $H_{C1}(0) = 3.36$ T, extrapolated from the phase diagram, and $H_{C2}(0) \approx 21$ T, H_A and H_E are estimated to 0.54 T and 10.8 T. From these molecular fields, an estimation of the magnetic anisotropy and the exchange interactions can be given: $|D|/k_B = 0.14$ K and $zJ'/k_B \approx -2.9$ K, justifying the weak anisotropy limit, $|zJ'| \gg |D|$ (with $g\mu_B SH_A = 2DS^2$ and $g\mu_B SH_E = 2|zJ'|S^2$). Note that the estimated magnetic exchange in the FeBr_4^- salt is about twice as large as that estimated for the FeCl_4^- salt, likely explaining the observation of the ordered magnetic ground state of the former.

These magnetic analyses are indeed consistent with the X...X contact distances observed in the structures of both compounds. The closest X...X interactions occur between inversion-related FeX_4^- anions at 3.409(1) and 3.482(1) Å for the FeCl_4^- and FeBr_4^- salts (Fig. 7 and Fig. S17), respectively. These distances correspond to RR values of 0.97 and 0.94, indicating stronger interactions between FeBr_4^- anions. Moreover, the next closest Cl...Cl distances in the FeCl_4^- salt amount to 4.122(5) Å along the crystallographic a direction and 4.425(3) Å in the bc plane. The equivalent Br...Br distances in the FeBr_4^- salt are shorter, 4.058(5) and 4.254(3) Å, despite the larger radius of Br. Taken together, the shorter and more effective Br...Br contacts in three dimensions in the FeBr_4^- salt explain the stabilization of an 3D antiferromagnetic order, whereas the relatively longer Cl...Cl contacts in the FeCl_4^- salt limit the interactions to short-range correlations, thereby inhibiting the development of long-range magnetic order. The origin of such antiferromagnetic interactions has been attribu-



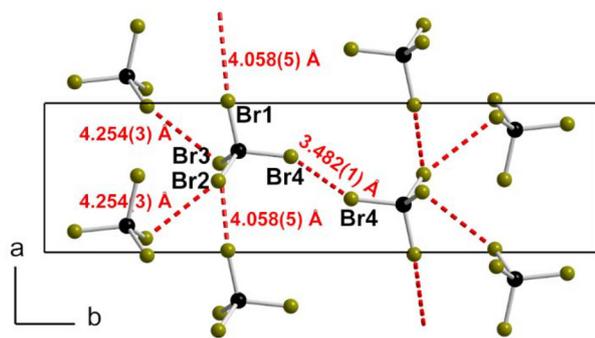


Fig. 7 Detail of the Br...Br interaction network in (1)(FeBr₄).

ted in some instances to so called π -d interactions, where the cation radicals would mediate indirect interactions between the $S = 5/2$ species.²³ However, the short Br...Br and Cl...Cl interactions found here lead us to rule out this possibility. On the other hand, a CCDC search for halogen-halogen intermolecular contacts between MX_4^- anions ($M = Fe, Ga; X = Cl, Br$) shows that the averaged $X...X$ distances amount to 3.516 Å and 3.552 Å in $GaCl_4^-$ and $FeCl_4^-$ salts, to 3.602 Å and 3.629 Å in $GaBr_4^-$ and $FeBr_4^-$ respectively. The notably shorter distances found here in (1)(FeCl₄) and particularly in (1)(FeBr₄) [3.482(1) Å] demonstrate that the $Se...X$ ChB interactions with the 1^{+} cation radicals play an important role in bringing close to each other the $S = 5/2$ metalate anions. Such effects were discussed in isostructural salts of $FeCl_4^-$ and $FeBr_4^-$ with tetramethylammonium²⁴ or 2-methylquinolinium²⁵ counter ions. In such systems and despite larger Br...Br than Cl...Cl intermolecular distances, stronger antiferromagnetic interactions are also observed with $FeBr_4^-$. Also, in cation radical salts of tetrathiafulvalenes derivatives with $FeCl_4^-$ and $FeBr_4^-$,²⁶ the stronger antiferromagnetic interaction with the latter (and stabilization of an antiferromagnetic ground state) was indeed attributed to the increase of the “d-p mixing” between 3d orbitals of Fe and 4p orbitals of Br atoms and the large electron cloud of Br atom in the $FeBr_4^-$ salt,²⁷ which enhance the intermolecular magnetic interaction through halogen atoms compared to the $FeCl_4^-$ salt.

To cross-check the presence of the magnetic phase transition at low temperatures, heat capacity measurements were performed on both compounds between 2 and 50 K. As shown in Fig. 8, a reproducible λ -type feature is observed for the $FeBr_4^-$ salt, confirming the presence of an ordered magnetic ground state. In contrast, the appearance of a broad feature around 2 K in the $FeCl_4^-$ salt is likely due to the short-range order effect,²⁸ which is consistent with the magnetic data (Fig. S18). In order to further analyze these calorimetric measurements, the magnetic component of the heat capacity (C_{pm}) was extracted by subtracting the baseline, which should mainly correspond to the lattice contribution and was modeled to an empirical polynomial expression. While this correction was reasonably applied to the $FeBr_4^-$ salt (Fig. 8), the broad low temperature rise of C_p in the $FeCl_4^-$ salt made

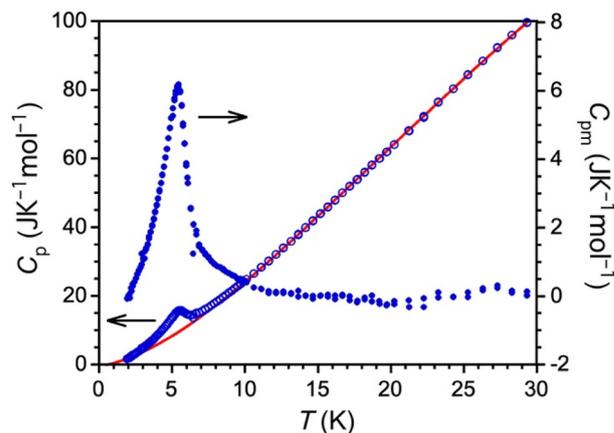


Fig. 8 Open circles: temperature dependence of the heat capacity, C_p , per mole of the $FeBr_4^-$ salt measured on a polycrystalline sample under zero applied field. The red solid line corresponds to the empirical polynomial base line used to determine the non-magnetic background of the heat capacity ($C_{p,background}$). Full circles: temperature dependence of the magnetic component (C_{pm}) of the heat capacity deduced from $C_{pm} = C_p - C_{p,background}$.

the fit inherently less precise, which in turn could lead to significant errors in the C_{pm} . The resulting C_{pm} vs. T plots reveal a broad feature centered around 2.7 K for the $FeCl_4^-$ salt (Fig. S19), while a sharp λ -type anomaly with a maximum at 5.5 K is observed for the $FeBr_4^-$ salt. Numerical integration of the C_{pm} between 2 and 15 K yields an associated magnetic entropy (S_m), which reaches saturation values of 20.9 and 16.5 $J K^{-1} mol^{-1}$ for the $FeCl_4^-$ and $FeBr_4^-$ salts, respectively (Fig. S20–S21). The estimated entropy gain for the $FeBr_4^-$ salt is very close to $R \ln 6 = 14.9 J K^{-1} mol^{-1}$, the value expected for the spin entropy ($S = 5/2$ Fe^{III} centers), confirming the bulk magnetic order of the Fe^{III} spins. The pronounced entropy contribution observed in the $FeCl_4^-$ salt can be ascribed to factors such as the imprecise estimation of the base line correction (*vide supra*) and/or contributions beyond the purely magnetic component. Another plausible origin is the presence of structural disorder within the system, which not only enhances the overall entropy but also inhibits the stabilization of long-range magnetic order.

Conclusion

We have demonstrated that the electron-rich *peri*-diselenide donor, 2,7-dimethoxynaphthalene *peri*-diselenide (1), can be oxidized into stable radical cations to afford 1:1 salts with FeX_4^- and GaX_4^- ($X = Cl, Br$) anions. Theoretical calculations reveal a pronounced localization of the HOMO and spin density on the selenium atoms, where σ -holes simultaneously emerge to engage in chalcogen bond (ChB) with the anions. Structural analysis confirms the presence of short and directional $Se...X$ ($X = Cl, Br$) ChB interactions around the diselenide bridge with both FeX_4^- and GaX_4^- anions, which effec-

tively bring the anions into close proximity. In addition, strong dimerization of the radical is observed along the stacks of $1^{+\cdot}$, leaving the FeX_4^- anions as the sole contributors to the magnetic behavior. Magnetic susceptibility and heat capacity measurements suggest that the FeBr_4^- salt undergoes a 3D antiferromagnetic order below $T_N = 5.9$ K, whereas the FeCl_4^- salt exhibits only short-range correlations above 1.85 K. The stronger magnetic interactions in the FeBr_4^- salt are rationalized by shorter Br...Br contacts. Taken together, these findings demonstrate that the oxidized cation of electron rich diselenides can act as efficient ChB donors, providing a new strategy to control supramolecular organization with magnetic anions and opening perspectives for the design of molecular materials with emergent properties.

Author contributions

H. P. P. synthesized and crystallized the compounds, O. J. performed the crystallographic studies and theoretical calculations, M. R., R. C. and I.-R. J. conducted and analyzed the magnetic and the calorimetric studies, I.-R. J. and M. F. supervised the work. All the authors contributed to the preparation and writing of the manuscript.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information is available: Experimental and synthetic methods, crystallographic and theoretical calculation details, powder X-ray diffraction and magnetostructural correlation data, and additional structural, magnetic, and thermodynamic property data. See DOI: <https://doi.org/10.1039/d6dt00277c>.

CCDC 2497447 (1)(FeCl_4), 2497448 (1)(GaCl_4), 2497449 (1)(GaCl_4 _B), 2497450 (1)(FeBr_4) and 2497451 (1)(GaBr_4) contain the supplementary crystallographic data for this paper.^{29a-e}

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