¹¹³Cd Solid-State NMR at 21.1 T Reveals the Local Structure and Passivation Mechanism of Cadmium in Hybrid and All-Inorganic Halide Perovskites

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Supporting Information Placeholder

ABSTRACT: Cadmium doping has recently emerged as an efficacious strategy for defect suppression and band gap tuning in hybrid as well as all-inorganic halide perovskites. However, the cadmium speciation in these materials is unknown. Here, we use high field cadmium-113 NMR spectroscopy in conjunction with chemical shift calculations by fully relativistic density functional theory to establish the phase composition of cadmium-doped lead halide perovskites. We find that cadmium does not incorporate into the 3D perovskite lattice of MA- and FA-based lead halide perovskites (MAPbI₃ and the gold-standard triple cation mixed-halide composition). Instead, it forms separate, cadmium-rich non-perovskite phases for as little as 1 mol% Cd²⁺ doping. Conversely, we find that cadmium can incorporate into the 3D perovskite lattice of CsPbBr₃ *via* homovalent Pb²⁺ substitution up to around 10 mol%. Our results thus reveal the atomic-level mechanism of this recently developed defect passivation strategy.

Substitutional doping has emerged as one of the most versatile strategies for tuning the optoelectronic properties of halide perovskites,¹ leading to their widespread use in light emission^{2,3} and harvesting^{4–6} applications. The 3D halide perovskite structure, ABX₃, is composed of monovalent A-site cations (e.g. methylammonium, (CH₃NH₃)⁺, MA), formamidinium (CH(NH₂)₂⁺, FA), cesium) and divalent B-site cations (e.g. Pb²⁺, Sn²⁺), forming [BX₆]^{4–} octahedra, where X=I, Br and/or Cl. Modulation of halide perovskite properties has been achieved by main group^{5,7–10} transition metal^{10–12} and lanthanide^{13–15} doping, as well as using a wide range of organic cations and neutral molecules.^{16–18}

Defect passivation is currently one of the key challenges and most widely used strategies for improving the performance of halide perovskites in optoelectronic devices.¹⁸ Cadmium doping has recently emerged as an effective means of suppression of atomic vacancies and band gap tuning in both hybrid^{8,19,20} as well as all-inorganic²¹ perovskites through B-site alloying. Figure 1 schematically shows the structural model for B-site substitutional doping of lead halide perovskites with Cd²⁺. While the optoelectronic modulation effects have been substantial, the atomic-level mechanism of Cd²⁺ passivation has not yet been established experimentally.

While the dopant incorporation, leading to homo- or heterovalent substitution on the A- or B-site can sometimes be evaluated using X-ray diffraction, the effect is often subtle, especially for low dopant concentrations. In addition, phase segregation in mixed-

halide compositions inevitably leads to changes in the original halide ratio and in turn the lattice constant, making it difficult to disentangle it from the effect of dopant incorporation.^{22,23}

Solid-state NMR has proven to be a particularly useful method for probing dopant incorporation into halide perovskites, as it allows to establish the phase composition by either directly probing the doping ion and its local structure or indirectly by detecting the effect the dopant has on the surrounding NMR-active nuclei.^{24,25} For example, we have previously shown that rubidium,²² potassium,²⁶ barium²³ and cobalt²⁷ do not incorporate into the lattice of 3D halide perovskites, while manganese,²⁷ europium¹⁴ and guanidinium²⁸ do incorporate. In the same vein, dimethylammonium²⁹ and copper¹² incorporation has been evidenced and halide mixing has been extensively studied in different all-inorganic³⁰ and hybrid^{25,31–34} halide perovskites.

Figure 1. Schematic representation of B-site substitutional doping of lead halide perovskites with Cd²⁺.

Cadmium-113 (spin $I = 1/2$, 12.2% abundant) has a receptivity 8 times higher than that of ¹³C and has been widely used to experimentally and theoretically study inorganic compounds,³⁵ molecular complexes,^{36–39} nanoparticles,^{40–42} MOFs⁴³, metal ion binding sites in proteins^{44,45}. Cadmium-111 (spin $I = 1/2$, 12.8% abundant) has similar receptivity to that of cadmium-113 and is occasionally used as an alternative, yielding identical structural information.⁴⁶ Cadmium-113 typically exhibits chemical shift anisotropy on the order of 10-300 ppm in inorganic cadmium compounds³⁵ and up to 600 ppm in coordination complexes⁴⁷, which is substantially reduced by magic angle spinning (MAS) at moderate spin rates (~20 kHz).

Here, we use very high field (21.1 T) cadmium-113 solid-state MAS NMR to establish for the first time the atomic-level

microstructure of cadmium-containing phases in Cd-doped halide perovskites. We find that cadmium does not incorporate into MA- and FA-based hybrid materials and quantitatively separates into cadmium-rich non-perovskite phases for as little as 1 mol% Cd^{2+} . On the other hand, we find that cadmium incorporates into the all-inorganic CsPbBr_3 perovskite, replacing up to around 10 mol% of Pb^{2+} on the B site.

All the materials investigated here were prepared using solid-state mechanosynthesis, which is a well-established, solvent-free synthetic method for preparing a broad range of organic and inorganic materials,⁴⁸ including high-quality lead halide perovskites.^{32,33,49–51} Previous extensive studies on organic and inorganic mechanosynthesis have shown that the large increase in concentration and high energy input may lead to metastable (kinetic) products inaccessible *via* solution processing.^{52–54} That said, in both approaches, halide perovskites are thermally annealed after synthesis, either to drive off the solvent or to remove grinding-induced defects, thereby favoring thermodynamic products. Indeed, we have previously found that solution processing leads to identical products as solvent-free solid-state synthesis for pure-phase materials, although residual solvent coordination may introduce disorder.^{22,26,28} Liquid-assisted mechanosynthesis is a convenient way of introducing solvent into mechanochemical preparations, with the limited amount being easier to drive off during high-temperature annealing.^{55–57} We also use the liquid-assisted protocol here to mimic the effect of DMSO/DMF-based solution processing.

MAPbI₃ doped with Cd²⁺

Figure 2 shows ¹¹³Cd MAS NMR echo-detected spectra of materials pertinent to the question of cadmium incorporation into MAPbI₃. The doping precursor, CdI₂, yields a resonance at -713 ppm (full width at half maximum, fwhm 12 ppm, analyzed prior to apodization) and is characteristic of octahedrally coordinated $[\text{CdI}_6]^{4-}$ (fig. 2a). The doping precursor could conceivably react with PbI₂ to form a mixed-metal halide, $\text{Cd}_{1-x}\text{Pb}_x\text{I}_2$, during the solid-state synthesis. We evaluate this possibility by preparing $\text{Cd}_{1-x}\text{Pb}_x\text{I}_2$ ($x=0.10$ and 0.50) and find that these materials do indeed form, leading to a slight shift and significant broadening (-715 ppm, fwhm 14 ppm and -718 ppm, fwhm 24 ppm for $x=0.10$ and 0.50 , respectively), consistent with the introduction of Cd/Pb chemical disorder in the mixed Cd-Pb halides, while the octahedral Cd coordination is preserved (fig. 2b, c). Substitutional doping of MAPbI₃ with Cd²⁺, represented formally as $\text{MAPb}_{1-x}\text{Cd}_x\text{I}_3$, (for $x=0.20$, 0.10 , 0.05 and 0.02), leads to the appearance of a new tetrahedrally coordinated $[\text{CdI}_4]^{2-}$ environment (103 ppm, fwhm ~5-20 ppm) which is not consistent with B-site incorporation of Cd²⁺ into the octahedra-based perovskite structure (fig. 2d-g). The same resonance is obtained when the material is prepared in the presence of the DMF:DMSO (4:1 v/v) mixture, commonly used for the fabrication of perovskite solar cells. This result confirms that the presence of the solvent does not affect the structure of the resulting cadmium-containing phase. There is only one known cadmium-rich phase in the MAI-CdI₂ phase diagram: MA_2CdI_4 .⁵⁸ The ¹¹³Cd MAS NMR signature of this phase (fig. 2i) matches exactly those of the Cd-doped MAPbI₃ materials (fig. 2d-h), confirming that *there is no incorporation of Cd²⁺ into the 3D perovskite structure of MAPbI₃*. Instead, Cd²⁺ separates into the non-perovskite methylammonium iodocadmate, MA_2CdI_4 . We confirm this result by carrying out fully relativistic DFT calculations of ¹¹³Cd chemical shifts, which yield extreme values, which are physically unreasonable, for both homovalent Cd²⁺-for- Pb²⁺ and aliovalent Cd²⁺-for-MA substitution (see *Details of DFT Calculations*, Table S4, S7 and Figure S7 in the Supplementary Information). We also note that the hypothetical homovalent Cd²⁺/Pb²⁺ mixing in the non-perovskite MA_2CdI_4 does not occur, since it would lead to disorder and considerable broadening (*vide infra*) of the ¹¹³Cd signal in the $\text{MAPb}_{1-x}\text{Cd}_x\text{I}_3$ compositions, which is not observed

experimentally (cf. fig. 2g and 2i), even though DFT predicts potential stability of Cd²⁺-for-Pb²⁺ substitution in this case (see *Details of DFT Calculations*, Table S6, S9 and Figure S7). No incorporation of Cd²⁺ into MAPbI₃ is consistent with the result previously reported by Dunlap-Shohl et al.²⁰ The corresponding XRD patterns are reported in Fig. S1.

Figure 2. ¹¹³Cd MAS NMR spectra at 21.1 T, 17 kHz and RT of bulk cadmium-containing perovskite and non-perovskite compositions: (a) CdI₂, (b) $\text{Cd}_{0.90}\text{Pb}_{0.10}\text{I}_2$, (c) $\text{Cd}_{0.50}\text{Pb}_{0.50}\text{I}_2$, (d) $\text{MAPb}_{0.80}\text{Cd}_{0.20}\text{I}_3$, (e) $\text{MAPb}_{0.90}\text{Cd}_{0.10}\text{I}_3$, (f) $\text{MAPb}_{0.95}\text{Cd}_{0.05}\text{I}_3$, (g) $\text{MAPb}_{0.98}\text{Cd}_{0.02}\text{I}_3$, (h) solvent-assisted (DMF:DMSO 4:1 v/v) $\text{MAPb}_{0.95}\text{Cd}_{0.05}\text{I}_3$, (i) MA_2CdI_4 (CSD identifier: ZEHVEQ), (j) MA_2CdI_4 (total amount of Cd²⁺ in the sample: 3 μmol). The line broadening parameters used for plotting the spectra are summarized in Table S1. The asterisks indicate spinning sidebands.

Importantly, the ¹¹³Cd spectrum of $\text{MAPb}_{0.98}\text{Cd}_{0.02}\text{I}_3$, yielded a signal-to-noise (SNR) of 6 after 20 hours of acquisition with the sample containing only 0.4 μmol of Cd²⁺ (fig. 2g). In a separate experiment, a sample containing 3.0 μmol of Cd²⁺ yielded an SNR of 10 after 17 hours of acquisition (fig. 2j), demonstrating the comparatively high sensitivity of ¹¹³Cd MAS NMR under these experimental conditions (high magnetic field and MAS) and

confirming that it is possible to detect all cadmium-containing environments present at the ~ 1 mol% level. We note that low temperature ^{113}Cd measurements could in principle be used to improve detection sensitivity further. However, we found that carrying out the measurements at 100 K leads to significantly broadened spectra which, in conjunction with slower possible MAS rates, leads to poorer spectral resolution (Fig. S5). We also note that the ^{113}Cd chemical shift of MA_2CdI_4 is strongly temperature dependent (ca. 0.23 ppm/K).

Mixed-cation and mixed-halide perovskites doped with Cd^{2+}

The highest efficiency perovskite solar cells are currently based on mixed-cation and mixed-halide materials, such as $(\text{Cs}, \text{MA}, \text{FA})\text{Pb}(\text{I}, \text{Br})_3$.^{59–62} The incorporation of Cd^{2+} into these multi-component materials may lead to the formation of a variety of cation- and halide-disordered cadmium-containing phases. Figure 3a-f shows a library of ^{113}Cd MAS NMR spectra of the reference cadmium-containing phases featuring tetrahedral $[\text{CdI}_4]^{2-}$, tetrahedral $[\text{CdBr}_4]^{2-}$ and octahedral $[\text{CdBr}_6]^{4-}$ units.

Figure 3. ^{113}Cd MAS NMR echo spectra at 21.1 T, 17 kHz and RT of bulk cadmium-containing perovskite and non-perovskite compositions: (a) MA_2CdI_4 , (b) FA_2CdI_4 , (c) MA_2CdBr_4 (CSD identifier: MAMCDB01), (d) FA_2CdBr_4 , (e) MACdBr_3 (CSD identifier: AMPRLC01)⁶³ (f) FACdBr_3 , (g) $\text{MA}_2\text{CdI}_{3.4}\text{Br}_{0.6}$, (h) $\text{FA}_2\text{CdI}_{3.4}\text{Br}_{0.6}$, (i) $\text{Cs}_{0.05}\text{MA}_{0.15}\text{FA}_{0.80}\text{Pb}_{0.99}\text{Cd}_{0.01}\text{I}_{2.55}\text{Br}_{0.45}$, (j) $\text{CsPb}_{0.90}\text{Cd}_{0.10}\text{Br}_3$. ICSD collection codes: 24483 (CsCdBr_3) and

100592 (Cs_2CdBr_4). The corresponding XRD patterns are reported in Fig. S2 and S3.

We see that the ^{113}Cd chemical shift is largely determined by the type of halide and coordination geometry while the organic cation (MA vs. FA) has a significantly smaller effect: MA_2CdI_4 (103 ppm, fwhm 8.5 ppm), FA_2CdI_4 (72 ppm, fwhm 6.5 ppm), MA_2CdBr_4 (386 ppm, fwhm 5.5 ppm), FA_2CdBr_4 (354 ppm, fwhm 3.0 ppm), MACdBr_3 (-77 ppm, fwhm 4.0 ppm), FACdBr_3 (-91 ppm, fwhm 4.0 ppm). We also note that ^{113}Cd T_1 relaxation times in iodo- and bromocadmates are considerably longer compared the corresponding haloplumbates and halostannates.^{31,64}

The introduction of two halides (I, Br) leads to halide disorder which manifests itself by the presence of up to 5 distinct signals, corresponding to mixed I/Br coordination environments with different I:Br ratios (fig. 4). The intensity of these discrete signals is proportional to the relative population of each of the 5 coordination environments: $[\text{CdI}_4]^{2-}$, $[\text{CdI}_3\text{Br}]^{2-}$, $[\text{CdI}_2\text{Br}_2]^{2-}$, $[\text{CdI}\text{Br}_3]^{2-}$, $[\text{CdBr}_4]^{2-}$, and consistent with random distribution of halides (Figure S8). An analogous pattern has been previously observed in the case of CdBrCl .³⁵ For the 3:4:0.6 ratio of I:Br, commonly used in the fabrication of perovskite solar cells, the corresponding MA- and FA-based halocadmiate phases exhibit a pattern of 3 resonances with an approximate ratio of 1:3:4 (fig. 3g and h, respectively): $\text{MA}_2\text{CdI}_{3.4}\text{Br}_{0.6}$ (262, 188 and 107 ppm, fwhm 16.5, 12.0, 12.0 ppm), $\text{FA}_2\text{CdI}_{3.4}\text{Br}_{0.6}$ (232, 157 and 75 ppm, fwhm 16.5, 15.0, 11.5 ppm).

Figure 4. ^{113}Cd MAS NMR echo spectra at 21.1 T, 17 kHz and RT of bulk cadmium-containing mixed-halide non-perovskite compositions: (a) FA_2CdI_4 , (b) $\text{FA}_2\text{CdI}_{3.4}\text{Br}_{0.6}$, (c) $\text{FA}_2\text{CdI}_{2.0}\text{Br}_{2.0}$, (d) FA_2CdBr_4 .

The introduction of 1 mol% of Cd^{2+} into the triple-cation double-halide perovskite material (Fig. 3i), as reported by Saidaminov et al.,⁸ leads to the formation of tetrahedrally coordinated cadmium environments which match a mixture of the non-perovskite cadmium-rich $\text{MA}_2\text{CdI}_{3.4}\text{Br}_{0.6}$, $\text{FA}_2\text{CdI}_{3.4}\text{Br}_{0.6}$ as well as mixed-cation $\text{MA}_{1-x}\text{FA}_x\text{CdI}_{3.4}\text{Br}_{0.6}$ whose chemical shifts falls in the range between those of the pure MA and pure FA mixed-halide halocadmates. *This result demonstrates that there is no Cd^{2+} incorporation into the mixed-cation, mixed-halide 3D perovskite phase of the triple-cation composition at the ~ 1 mol% level.* Interestingly, successful Cd^{2+}

incorporation onto an octahedral site *via* homovalent Pb^{2+} substitution has been previously concluded based on XPS data recorded on a single crystal of this material.⁸ We note, however, that XPS is strictly surface-sensitive and readily detects surface-adsorbed species. Solid-state NMR, on the other hand, probes the bulk of the material. This complementarity highlights the critical need for atomic-level characterization of new halide perovskite dopants. Since the resulting cadmium-rich phase contains mixed halides, we conclude that the halide composition of the 3D perovskite phase may be affected due to cadmium doping. Our result suggests that the beneficial effect of cadmium addition may therefore be related to halide management^{5,7} rather than its incorporation into the 3D perovskite structure.

All-inorganic CsPbBr_3 doped with Cd^{2+}

Cadmium incorporation has also been reported in the case of the all-inorganic CsPbBr_3 perovskite, where it leads to changes in the optical response of the material.²¹ Figure 3j shows a ^{113}Cd MAS NMR spectrum of $\text{CsPb}_{0.90}\text{Cd}_{0.10}\text{Br}_3$. In this case, the possible non-perovskite phases are as follows: CdBr_2 (-24 ppm, unresolved in NMR but absent in XRD), Cs_2CdBr_4 (419 ppm, small amount present), CsCdBr_3 (-42 ppm, unresolved in NMR but absent in XRD). However, in addition to these, the spectrum contains a very broad signal (-110 ppm, fwhm 135 ppm) of a new octahedral $[\text{CdBr}_6]^{4-}$ environment, corresponding to Cd^{2+} incorporated into the perovskite lattice of CsPbBr_3 . Fully relativistic DFT ^{113}Cd chemical shift calculations corroborate this assignment. While aliovalent Cd^{2+} -for- Cs^+ substitution again leads to extreme, physically unreasonable, calculated chemical shift values, we find that homovalent Cd^{2+} -for- Pb^{2+} substitution leads to ^{113}Cd chemical shifts in the range between -30 and -190 ppm (see *Details of DFT Calculations*, Table S5, S8 and Figure S7 in the Supplementary Information), which is in excellent agreement with the experimentally observed broad signal at -110 ppm. The unusually high width of this cadmium resonance is caused by B-site disorder: there are multiple possible statistical arrangements of the neighboring $[\text{PbBr}_6]^{4-}$ and $[\text{CdBr}_6]^{4-}$ octahedra, which are present simultaneously leading to a distribution of local structures. This result is consistent with the previous conclusions based on HAADF STEM mapping.²¹ In this case, the optoelectronic modulation is therefore caused by homovalent substitution of Pb^{2+} by Cd^{2+} inside the 3D perovskite lattice.

Indirect detection of Cd^{2+} doping through other nuclei

We finally note that other NMR-active elements can be used to indirectly probe the incorporation of cadmium into halide perovskites. In particular, ^{207}Pb chemical shifts have been shown to be highly sensitive to the halide coordination environment of Pb^{2+} ,^{25,31–33,65} although much less affected by the type of A-site^{26,33} and B-site⁶⁶. ^{13}C chemical shifts are a sensitive probe of A-site cation alloying^{28,29,67} and phase-purity in passivated 3D and 2D/3D perovskites.^{68–70} We have recently shown that ^{14}N MAS NMR is a highly sensitive probe of the cubooctahedral symmetry of the perovskites, which is probed by the fast picosecond-timescale reorientation of the A-site cation.^{67,71,72} B-site replacement of Pb^{2+} (ionic radius: 129 pm) with Cd^{2+} (110 pm) should lead to a noticeable change in the overall cubooctahedral symmetry. However, no change in the ^{14}N pattern shape is observed (fig. 5a, b), corroborating no cadmium incorporation into MAPbI_3 , consistent with the ^{113}Cd MAS NMR result described above. Similarly, ^{133}Cs MAS NMR can be used to probe the local environment of cesium in the undoped and Cd-doped CsPbBr_3 (fig. 5c, d). Consistent with cadmium incorporation into the 3D perovskite lattice of CsPbBr_3 , the ^{133}Cs resonance broadens owing to the introduction of B-site disorder, i.e. a statistical distribution of neighboring $[\text{PbBr}_6]^{4-}$ and $[\text{CdBr}_6]^{4-}$ octahedra, which leads to a broad continuum of slightly different local cesium environments. Our group and others have previously reported analogous disorder-

induced effects related to A-site²² and halide mixing^{14,30,73} in cesium-containing halide perovskites.

Figure 5. Indirect detection of cadmium doping using ^{14}N and ^{133}Cs MAS NMR spectra at 11.7 T, 5 kHz and RT. ^{14}N of (a) MAPbI_3 , (b) $\text{MAPb}_{0.95}\text{Cd}_{0.05}\text{I}_3$. ^{133}Cs of (c) CsPbBr_3 , (d) $\text{CsPb}_{0.90}\text{Cd}_{0.10}\text{Br}_3$.

In conclusion, using ^{113}Cd MAS NMR at 21.1 T, we have shown that Cd^{2+} is not incorporated into MAPbI_3 and FA-based mixed-cation (Cs, MA, FA) lead mixed-halide (I, Br) perovskites at doping levels as low as 1 mol%. Instead, it forms non-perovskite halocadmite phases: MA_2CdI_4 or $(\text{MA}/\text{FA})_2\text{Cd}(\text{I}, \text{Br})_4$, in contrast to previous conclusions on cadmium incorporation based on XPS. Consequently, we suggest that the passivation effect of cadmium may be related to halide management. The introduction of solvent (DMF:DMSO, 4:1 v/v) during the synthesis does not change the segregation behavior or the composition of the cadmium-rich phase. On the other hand, we find that Cd^{2+} is incorporated into the all-inorganic 3D perovskite phase of CsPbBr_3 , replacing Pb^{2+} on the B-site up to around 10 mol%, consistent with the previous HAADF STEM results. We hope that the determination of cadmium speciation provided by ^{113}Cd solid-state NMR will help guide the development of new, more efficient defect passivation strategies.

Associated Content

Supporting Information

Supplementary information (XRD, details of NMR experiments, additional NMR spectra, details of DFT calculations) is available in the online version of the paper. The NMR raw data are available from [link to be added on publication]. Requests for additional data and correspondence should be addressed to L.E.

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TOC:

¹¹³Cd Solid-state NMR at 21.1 T Reveals the Local Structure and Passivation Mechanism of Cadmium in Hybrid and All-Inorganic Halide Perovskites

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Experimental

Materials

The following materials were used: methylammonium iodide (DyeSol), formamidinium iodide (DyeSol), formamidinium bromide (DyeSol), PbI_2 (TCI, 99.99%), PbBr_2 (TCI), CdI_2 (AlfaAesar, 99.999%), CdBr_2 (AlfaAesar, 99.999%), CsI (AlfaAesar, 99.999%).

Perovskite mechanosynthesis

The precursors were stored inside a glove box under dry nitrogen. Microcrystalline perovskites were synthesized by grinding the reagents in an electric ball mill (Retsch Mixer Mill MM-200) for 30 min. at 25 Hz using a grinding jar (10 ml) and a ball ($\varnothing 10$ mm). The resulting powders were annealed at 130 °C (in the case of organic-inorganic perovskites) or at 130 °C (in the case of all-inorganic perovskites) for 5 minutes. The solvent-assisted preparation was annealed at 130 °C for 30 minutes to drive off the residual solvent.

The following amounts of reagents were used:

$\text{Cd}_{0.90}\text{Pb}_{0.10}\text{I}_2$: 0.330 g (0.90 mmol) CdI_2 , 0.46 g (0.10 mmol) PbI_2 .

$\text{Cd}_{0.50}\text{Pb}_{0.50}\text{I}_2$: 0.183 g (0.50 mmol) CdI_2 , 0.230 g (0.50 mmol) PbI_2 .

$\text{MAPb}_{0.80}\text{Cd}_{0.20}\text{I}_3$: 0.159 g (1.00 mmol) MAI, 0.452 g (0.80 mmol) PbI_2 , 0.007 g (0.20 mmol) CdI_2 .

$\text{MAPb}_{0.90}\text{Cd}_{0.10}\text{I}_3$: 0.159 g (1.00 mmol) MAI, 0.438 g (0.90 mmol) PbI_2 , 0.018 g (0.10 mmol) CdI_2 .

$\text{MAPb}_{0.95}\text{Cd}_{0.05}\text{I}_3$: 0.159 g (1.00 mmol) MAI, 0.415 g (0.95 mmol) PbI_2 , 0.037 g (0.05 mmol) CdI_2 .

$\text{MAPb}_{0.98}\text{Cd}_{0.02}\text{I}_3$: 0.159 g (1.00 mmol) MAI, 0.369 g (0.98 mmol) PbI_2 , 0.073 g (0.02 mmol) CdI_2 .

MAPbI_3 : 0.159 g (1.00 mmol) MAI, 0.461 g (1.00 mmol) PbI_2 .

Solvent-assisted $\text{MAPb}_{0.95}\text{Cd}_{0.05}\text{I}_3$: 0.159 g (1.00 mmol) MAI, 0.415 g (0.95 mmol) PbI_2 , 0.037 g (0.05 mmol) CdI_2 , 30 μl of DMF:DMSO (4:1 v/v).

MA_2CdI_4 : 0.318 g (2.00 mmol) MAI, 0.366 g (1.00 mmol) CdI_2 .

FA_2CdI_4 : 0.344 g (2.00 mmol) FAI, 0.366 g (1.00 mmol) CdI_2 .

MACdBr_3 : 0.112 g (1.00 mmol) MABr, 0.272 g (1.00 mmol) CdBr_2 .

FACdBr_3 : 0.125 g (1.00 mmol) FABr, 0.272 g (1.00 mmol) CdBr_2 .

$\text{MA}_2\text{CdI}_{3.4}\text{I}_{0.6}$: 0.318 g (2.00 mmol) MAI, 0.256 g (0.70 mmol) CdI_2 , 0.082 g (0.30 mmol) CdBr_2 .

$\text{FA}_2\text{CdI}_{3.4}\text{I}_{0.6}$: 0.344 g (2.00 mmol) FAI, 0.256 g (0.70 mmol) CdI_2 , 0.082 g (0.30 mmol) CdBr_2 . **$\text{FA}_2\text{CdI}_{2.0}\text{I}_{2.0}$** : 0.344 g (2.00 mmol) FAI, 0.272 g (1.00 mmol) CdBr_2 . **$\text{Cs}_{0.05}\text{MA}_{0.15}\text{FA}_{0.80}\text{Pb}_{0.99}\text{Cd}_{0.01}\text{I}_{2.55}\text{Br}_{0.45}$** : 0.013 g (0.05 mmol) CsI , 0.024 g (0.15 mmol) MAI, 0.122 g (0.71 mmol) FAI, 0.011 g (FABr), 0.066 g (0.18 mmol) PbBr_2 , 0.373 g (0.81 mmol) PbI_2 , 0.004 g (0.01 mmol) CdI_2 .

CsPbBr_3 : 0.213 g (1.00 mmol) CsBr , 0.367 g (1.00 mmol) PbBr_2 ,

$\text{CsPb}_{0.90}\text{Cd}_{0.10}\text{Br}_3$: 0.213 g (1.00 mmol) CsBr , 0.330 g (0.90 mmol) PbBr_2 , 0.027 g (0.10 mmol) CdBr_2 .

NMR measurements

Solid-state MAS NMR spectra of ^{113}Cd (199.8 MHz) were recorded on a Bruker Avance Neo 21.1 T spectrometer with a 3.2 mm CPMAS probe (room-temperature experiments) or a 3.2 mm LTMAS probe (100 K experiments). The ^{133}Cs (65.6 MHz) and ^{14}N (36.2 MHz) spectra were recorded on a Bruker Avance III 11.7 T spectrometer equipped with a CPMAS probe. Cesium-133 shifts were externally referenced to a 1 M aqueous solution of cesium chloride, using solid CsI ($\delta=271.05$ ppm) as a secondary reference.³⁰ Nitrogen-14 spectra were externally referenced to solid NH_4Cl (0 ppm) at 298 K. Cadmium-113 spectra were acquired using an echo sequence to eliminate distortions due to receiver dead time. The refocusing pulse was either a hard π or a tanh/tan (see ref. 25) pulse (as specified in Table S1), with the latter being used when the range of ^{113}Cd chemical shifts was too large to be covered by a single hard π pulse. The tanh/tan pulse had a duration of 58.8 μs and a bandwidth of 4 MHz. A pair of tanh/tan pulses were used to eliminate second-order phase distortion (i.e. $90^\circ - \text{tanh/tan} - \tau - \text{tanh/tan} - \tau - \text{acquire}$). For the saturation-recovery experiments, saturation was achieved by applying a train of 30 $\pi/2$ pulses spaced by 3 ms. No ^1H decoupling was used during the acquisition of the ^{113}Cd spectra since we found it does not lead to any noticeable improvement in resolution. Recycle delays were optimized based on the T_1 values measured for reference samples (given in Table S1). About 70 mg of material was used for each measurement, corresponding to a full 3.2 mm zirconia rotor. All ^{113}Cd measurements were carried out using the same spin rate and VT flow rate to account for spinning-induced sample heating (ca. +20 K at 17 kHz). The fitted ^{113}Cd peak positions reported in the main text have standard deviations on the order of 0.01 ppm. However, we note that the strong temperature dependence of ^{113}Cd chemical shifts (ca. 0.23 ppm/K in the range 100-300 K) together with possible temperature fluctuations on the order of ± 1 K lead to an experimental error of about ± 0.5 ppm on the reported ^{113}Cd chemical shifts.

The T_2^* calculated from the full width at half maximum of MA_2CdI_4 (237 μs) and MA_2CdBr_4 (238 μs) are nearly identical and considerably longer than the rotor period (58.8 μs). Since T_2^* is always less or equal to T_2' , we conclude that T_2' is not a limiting factor in comparing iodo- and bromostannates. This confirms that there is no appreciable difference in dephasing due to T_2' during the echo period. This is also corroborated by the fact that the intensity ratio of mixed I/Br coordination environments with different I:Br ratios closely matches the theoretical values predicted by the binomial distribution.

The NMR raw data are available from [\[link to be added on publication\]](#) in the TopSpin data format. Data are made available under the license CC-BY-4.0 (Creative Commons Attribution-ShareAlike 4.0 International).

XRD data

Powder X-ray diffraction patterns were recorded on an X'Pert MPD PRO (Panalytical) diffractometer equipped with a ceramic tube (Cu anode, $\lambda = 1.54060$ Å), a secondary graphite (002) monochromator and an RTMS X'Celerator (Panalytical) in an angle range of $2\theta = 5^\circ$ to 50° , by step scanning with a step of 0.02 degree.

Figure S1. Powder X-ray diffraction patterns of the materials reported in Figure 2 of the main text.

Figure S2. Powder X-ray diffraction patterns of the materials reported in Figure 3 of the main text.

Figure S3. Powder X-ray diffraction patterns of the materials reported in Figure 3 of the main text.

Figure S4. Powder X-ray diffraction patterns of the materials reported in Figure 4 of the main text.

Additional NMR data

Figure S5. ^{113}Cd MAS NMR spectra at 21.1 T, 12 kHz of bulk MA_2CdI_4 at 300 K (top, $T_1=5.7$ s) and 100 K (bottom, $T_1 = 3.8$ s).

Table S1. Acquisition and processing parameters used for the spectra in the main text.

¹¹³ Cd spectra							
composition	Figure	¹¹³ Cd T ₁ [s]	recycle delay [s]	number of scans	acquisition time [h]	Lorentzian apodization [Hz]	Echo refocusing pulse
CdI ₂	2	114	160	16	0.7	200	hard π
Cd _{0.90} Pb _{0.10} I ₂		-	160	40	1.8	200	hard π
Cd _{0.50} Pb _{0.50} I ₂		-	160	64	2.8	500	hard π
MAPb _{0.80} Cd _{0.20} I ₃		-	5	128	0.2	1000	hard π
MAPb _{0.90} Cd _{0.10} I ₃		-	5	18228	25.3	1000	tanh/tan
MAPb _{0.95} Cd _{0.05} I ₃		-	5	2255	3.1	1000	tanh/tan
MAPb _{0.98} Cd _{0.02} I ₃		-	5	14360	19.9	1000	tanh/tan
Solvent-assisted MAPb _{0.95} Cd _{0.05} I ₃		-	10	5212	14.5	1000	tanh/tan
MA ₂ CdI ₄		5.7	7	256	0.5	200	hard π
MA ₂ CdI ₄ (3 μ mol)		-	5	12368	17.2	1000	hard π
FA ₂ CdI ₄	3	6.3	8	1024	2.3	200	hard π
MA ₂ CdBr ₄		87	100	16	0.4	100	tanh/tan
FA ₂ CdBr ₄		-	100	64	1.8	500	tanh/tan
MACdBr ₃		11.3	15	140	0.6	100	tanh/tan
FACdBr ₃		82	60	44	0.7	100	tanh/tan
MA ₂ CdI _{3.4} Br _{0.6}		3.6	5	456	0.6	500	tanh/tan
FA ₂ CdI _{3.4} Br _{0.6}		10.7	20	260	1.4	400	tanh/tan
Cs _{0.05} MA _{0.15} FA _{0.80} Pb _{0.99} Cd _{0.01} I _{2.55} Br _{0.45}		-	5	78199	108.6	3000	tanh/tan
CsPb _{0.90} Cd _{0.10} Br ₃		-	30	2172	18.1	3000	tanh/tan
FA ₂ CdI _{2.0} Br _{2.0}	4	-	10	928	2.6	500	tanh/tan

¹⁴N spectra

composition	Figure	recycle delay [s]	number of scans	acquisition time [h]	Lorentzian apodization [Hz]
MAPbI ₃	5	0.3	4448	0.4	50
MAPb _{0.95} Cd _{0.05} I ₃		0.3	18824	1.6	50

¹³³Cs spectra

composition	Figure	recycle delay [s]	number of scans	acquisition time [h]	Lorentzian apodization [Hz]
CsPbBr ₃	5	26	128	0.9	10
CsPb _{0.90} Cd _{0.10} Br ₃		26	128	0.9	50

Details of DFT calculations

Reference calculations for DFT chemical shifts

Typical DFT quantum chemical methods do not directly calculate the chemical shifts (δ_{DFT}). Instead, they are used to calculate the magnetic shieldings (σ_{DFT}), which are then transformed to chemical shifts using the linear relation,

$$\delta_{exp} = \sigma_{ref} - b\sigma_{DFT}, \quad \text{Equation S1}$$

where σ_{ref} and b are fit using calculated magnetic shielding values from known reference compounds. Note, that it would also be possible to calculate σ_{ref} from the same compound as is used to reference the experimental values. However, this would correspond to using only one reference compound. It has been shown that using multiple reference compounds can significantly lower the calculation error. Further note that the slope (b) should be fixed at unity for an ideal case but is typically used to account for systematic errors within calculations, including incomplete basis sets and nuclear quantum effects. [1]

Here, we investigate the influence of different reference systems on the accuracy of DFT calculated ^{113}Cd chemical shifts. For this, we consider three distinct sets of reference calculations.

- A. A set of ionic salts containing ^{113}Cd . These references are relatively fast to calculate, due to their relatively simple crystal structure. However, contrary to the investigated perovskites, they do not contain organic molecules.
- B. A set of metal-organic-framework (MOF) structures. These structures contain similar atoms as the perovskite structures. However, their crystal structures are quite different.
- C. A set of reference perovskites. All the investigated reference structures are listed in Table S2.

The Amsterdam Density Functional (ADF) suite [2-3] was used to perform the NMR chemical shift calculations within the DFT framework. For the calculations the GGA BP86 [4-5] functional including the Grimme dispersion correction [6] and relativistic effects up to spin-orbit couplings within the ZORA [7-9] approximation were used. All-electron triple- ζ basis sets with two polarization functions (TZ2P) were used in the calculations. The final clusters were generated as a central ^{113}Cd surrounded by at least three coordination shells (see Table S2). The clusters were set up analogously to the previous paper by Kubicki *et al.* [10] and in accordance with recent computational studies of systems including heavy atoms, [11-16] ensuring charge compensation and resulting in symmetry-adapted clusters. [17] Prior to the cluster generation, reference structures containing hydrogen atoms were relaxed using periodic DFT calculations with Quantum Espresso (QE) [18] and the generalized gradient approximation (GGA) functional PBE. [19] The DFT optimization includes the Grimme dispersion correction [6] and relativistic effects up to spin-orbit couplings. For every calculation we use a plane-wave maximum cut-off energy of 100 Ry and a 2x2x2 Monkhorst-Pack grid of k-points.[20]

All structures (^1H relaxed and extracted clusters) as well as the QE and ADF input and output files are given in the Supplementary Material.

Table S2. Source and modifications of the cluster structures used in the DFT reference calculations.

Original structure and experimental chemical shift reference	Extracted cluster	Modifications in periodic system (QE)	Reference set
<i>CdBr₂</i> [21]	Cd ₂₇ Br ₅₄	–	A) Ionic salts
<i>CdCl₂</i> [21]	Cd ₂₁ Cl ₄₂	–	A) Ionic salts
<i>CdF₂</i> [21]	Cd ₁₅ F ₃₀	–	A) Ionic salts
<i>CdI₂</i> [21]	Cd ₂₃ I ₄₆	–	A) Ionic salts
<i>MOF-4</i> [22]	Cd(μ_2 -Cl) ₂ (μ_2 -CO ₂)(py)(trz)	Relax ¹ H positions	B) MOFs
<i>MOF-27</i> [22]	Cd(μ_2 -CO ₂) ₂ (py)(trz) ₂	Relax ¹ H positions	B) MOFs
<i>MOF-12</i> [22]	Cd(trz) ₂ (H ₂ O) ₄	Relax ¹ H positions	B) MOFs
<i>MA₂CdI₄</i> [23]	MA ₂₆ Cd ₁₃ I ₅₄	Relax ¹ H positions	B) MOFs
<i>Cs₂CdCl₄</i> [21]	Cs ₃₄ Cd ₁₇ Cl ₆₈	–	C) Perovskites
<i>MA₂CdBr₄</i> [24]	MA ₁₈ Cd ₉ Br ₃₆	Relax ¹ H positions	C) Perovskites
<i>CsCdBr₃</i> [21]	Cs ₂₁ Cd ₂₁ Br ₆₃	–	C) Perovskites
<i>MACdBr₃</i> [24]	MA ₂₄ Cd ₁₁ Br ₄₈	Relax ¹ H positions	C) Perovskites

To investigate the influence of different reference systems on the accuracy of DFT calculated ¹¹³Cd chemical shifts, we use four linear regression models to estimate the parameters (slope and intercept) of Equation S1. For this we either only use set A) ionic salts, set B) MOFs, set C) perovskites, or D) all three sets, simultaneously. Figure S6 and Table S3, show the results for all four linear regression models. From Table S3, it is clear, that we obtain the best fit for each set, if we use the linear model determined exclusively on that set. E.g. for set C) perovskites, model C) decreases the expected RMSE by around 10 ppm (approximately 16 %) and for set B) MOFs, model B) even decreases the expected RMSE by around 30 ppm (approximately 60 %). Note, that set B) MOFs, exhibits a relatively narrow spread of ¹¹³Cd chemical shifts. For this reason, while model B) is able to accurately reproduce the chemical shifts of set B), it does not generalize well to the other reference sets. Further, we note that set A) ionic salts, which contains a relative broad spread of ¹¹³Cd chemical shifts, performs well for all three reference sets and nearly matches the performance of model D) all sets. These two models (A and D) also result in a slope (*b*) closest to unity. We also note, that while set C) has a relatively broad ¹¹³Cd chemical shift range, it doesn't contain any chemical shifts at very low ppm values and thus does not generalize well to set A). **This emphasizes the importance of using a representative reference set or at least a reference set, which is similar to the investigated structures.**

We thus use models C) perovskites, and D) all sets, for the subsequent ¹¹³Cd chemical shift calculations of the investigated perovskites.

Figure S6. Experimental chemical shifts plotted against DFT magnetic shielding. The different reference sets are shown as, A) ionic salts (blue circles), B) MOFs (green diamonds) and C) perovskites (yellow triangles). The best fit lines are calculated using only set A) ionic salts (blue), only set B) MOFs (green), only set C) perovskites (yellow) or D) all three sets (red). The slopes (b), intercepts (σ_{ref}) and root-mean-square-errors (RMSE) for each linear regression model are given in .

Table S3. Experimental chemical shifts and DFT calculated magnetic shielding and chemical shifts for the used reference structures.

Structure	DFT calculated magnetic shieldings (σ_{DFT}) / ppm	Experimental chemical shifts (δ_{DFT}) / ppm	DFT chemical shifts (δ_{DFT}) / ppm using set A) as reference	DFT chemical shifts (δ_{DFT}) / ppm using set B) as reference	DFT chemical shifts (δ_{DFT}) / ppm using set C) as reference	DFT chemical shifts (δ_{DFT}) / ppm using D) all sets
<i>CdBr₂</i> [21]	4271.1	-24	-107.3	-139.9	-66.0	-93.6
<i>CdCl₂</i> [21]	3941.4	184	185.4	294.5	166.7	187.3
<i>CdF₂</i> [21]	4308.0	-226	-140.1	-188.5	-92.1	-125.1
<i>CdI₂</i> [21]	4957.7	-713	-716.9	-1044.4	-550.6	-678.5
<i>MOF-4</i> [22]	4053.1	166.6	86.2	147.3	87.8	92.2
<i>MOF-27</i> [22]	4141.0	36.4	8.2	31.5	25.8	17.3
<i>MOF-12</i> [22]	4070.8	99.9	70.5	124.0	75.4	77.1
<i>MA₂CdI₄</i> [23]	3910.0	102.6	213.3	335.9	188.8	214.1
<i>Cs₂CdCl₄</i> [21]	3884.9	193	235.6	369.0	206.6	235.5
<i>MA₂CdBr₄</i> [24]	3727.1	386	375.7	576.8	317.9	369.9
<i>CsCdBr₃</i> [21]	4253.9	-42	-92.0	-117.2	-53.9	-78.9
<i>MACdBr₃</i> [24]	4314.4	-76.7	-145.7	-196.9	-96.6	-130.4
Results						
<i>Slope (b)</i>			0.89	1.32	0.71	0.85
<i>Intercept (σ_{ref}) / ppm</i>			3685.0	5486.9	2948.3	3545.2
<i>RMSE for set A) / ppm</i>			59.9	185.0	107.7	63.7
<i>RMSE for set B) / ppm</i>			52.0	18.0	48.0	46.3
<i>RMSE for set C) / ppm</i>			65.5	168.4	50.6	61.2
<i>RMSE for D) all sets / ppm</i>			60.5	152.7	74.2	58.7

DFT ^{113}Cd chemical shift and energy calculations

We computationally investigate the possibility of doping MAPbI_3 and CsPbBr_3 with Cd as well as the possibility of doping MA_2CdI_4 with Pb.

We start with the pure MAPbI_3 , CsPbBr_3 and MA_2CdI_4 structures, from where we extract super-cells containing four unit-cells (e.g. $\text{MA}_4\text{Pb}_4\text{I}_{12}$). For MAPbI_3 and CsPbBr_3 , we then generate super-cells where we replace one Pb with Cd. We additionally generate super-cells where we replace one Cs or MA with Cd. For MA_2CdI_4 we generate super-cells where we replace one Cd with Pb.

For all structures, we then calculate the relative DFT energy while either relaxing all atoms, relaxing only the replaced atom (Cd or Pb), or without relaxation. The DFT calculations are done using QE and the same parametrization as for the reference calculations. Note that the hydrogen positions of all initial structures were optimized prior to any further modifications. All investigated structures and applied modifications are listed in Tables S4-S6. Note for the energies of the non-optimized structures, we used the initial energies of the structure optimizations. All initial and modified structures as well as the QE input and output files are included in the Supplementary Material.

Table S4. Investigated modifications of the MAPbI_3 structure used in the DFT calculations.

Original structure	Doped structures (2x2x1 super-cell)	Modifications in periodic system (QE)	Lowest relative lattice energy (DFT) / eV / atom	Extracted cluster for ADF chemical shift calculations
<i>MAPbI₃</i>	<i>MAPbI₃</i>	Relax ^1H positions	595.2	–
	<i>MA₃CdPb₄I₁₂</i>	Relax ^1H positions in original structure	1322.0	<i>MA₁₈CdPn₈I₃₆</i>
	<i>MA₃CdPb₄I₁₂</i>	Relax ^1H positions in original structure Optimize ^{113}Cd position		<i>MA₁₈CdPn₈I₃₆</i>
	<i>MA₃CdPb₄I₁₂</i>	Optimize all atom positions		None, because very distorted structure
	<i>MA₄Pb₃CdI₁₂</i>	Relax ^1H positions in original structure	0.0	<i>MA₉Pb₆CdI₂₂</i>
	<i>MA₄Pb₃CdI₁₂</i>	Relax ^1H positions in original structure Optimize ^{113}Cd position		None, because equivalent to original structure
	<i>MA₄Pb₃CdI₁₂</i>	Optimize all atom positions		<i>MA₉Pb₆CdI₂₂</i>

Table S5. Investigated modifications of the CsPbBr₃ structure used in the DFT calculations.

Original structure	Doped structures (2x2x1 super-cell)	Modifications in periodic system (QE)	Lowest relative lattice energy (DFT) / eV / atom	Extracted cluster for ADF chemical shift calculations
CsPbBr₃	CsPbBr₃	Relax ¹ H positions	91.9	None
	Cs₃CdPb₄Br₁₂	Relax ¹ H positions in original structure	0.0	Cs ₁₈ CdPb ₈ Br ₃₆
	Cs₃CdPb₄Br₁₂	Relax ¹ H positions in original structure Optimize ¹¹³ Cd position		Cs ₁₈ CdPb ₈ Br ₃₆
	Cs₃CdPb₄Br₁₂	Optimize all atom positions		Cs ₁₈ CdPb ₈ Br ₃₆
	Cs₄Pb₃CdBr₁₂		429.0	Cs ₈ Pb ₂₂ Cd ₅ Br ₆₂
	Cs₄Pb₃CdBr₁₂	Optimize ¹¹³ Cd position		None, because equivalent to original structure
	Cs₄Pb₃CdBr₁₂	Optimize all atom positions		Cs ₈ Pb ₂₂ Cd ₅ Br ₆₂

Table S6. Investigated modifications of the MA₂CdI₄ structure used in the DFT calculations.

Original structure	Doped structures (2x2x2 super-cell)	Modifications in periodic system (QE)	Lowest relative lattice energy (DFT) / eV / atom	Extracted cluster for ADF chemical shift calculations
MA₂CdI₄	MA₂CdI₄	Relax ¹ H positions	40.1	MA ₂₄ Cd ₁₂ I ₄₈ (see reference calculations)
	MA₁₆Cd₇PbI₃₂	Relax ¹ H positions in original structure	0.0	MA ₂₄ Cd ₁₁ PbI ₄₈
	MA₁₆Cd₇PbI₃₂	Relax ¹ H positions in original structure Optimize ²⁰⁷ Pb position		MA ₂₄ Cd ₁₁ PbI ₄₈
	MA₁₆Cd₇PbI₃₂	Optimize all atom positions		MA ₂₄ Cd ₁₁ PbI ₄₈

For MAPbI_3 , we find that the doped structure with one Pb replaced by Cd has the lowest relative lattice energy and that the $\text{MA} \rightarrow \text{Cd}$ substituted structure has the highest relative lattice energy.

For CsPbBr_3 , we find that the doped structure with one Cs replaced by Cd has the lowest relative lattice energy and that the $\text{Pb} \rightarrow \text{Cd}$ doped structure has the highest relative lattice energy.

For MA_2CdI_4 , we find that the $\text{Cd} \rightarrow \text{Pb}$ doped structure has the lowest relative lattice energy. Note, that the relative lattice energies are only compared within the same original structure families.

In order to further investigate the doped perovskites, we calculate the ^{113}Cd chemical shifts of the doped structures using ADF. For the ADF calculations we use the same parametrization as for the reference DFT chemical shift calculations. The investigated clusters are also extracted in the same manner and are detailed in Tables S4-S6. Note, for the $\text{Cs}_8\text{Pb}_{25}\text{Cd}_2\text{Br}_{62}$ with the Cd – Cd in the 2nd coordination shell, we used the all-electron triple- ζ basis set with one polarization function (TZP) for the cesium atoms. Figure S7 shows some example clusters used in the ADF calculations. For the $\text{Cs}_3\text{CdPb}_4\text{Br}_{12}$ structures, we further investigate clusters containing exactly two Cd dopants, one with a Cd – Cd in the 2nd coordination shell and one with a Cd – Cd in the 4th coordination shell (see Figure S7, panels F and G). These structures were generated from the non-optimized $\text{Cs}_3\text{CdPb}_4\text{Br}_{12}$ structure. All extracted clusters as well as the ADF input and output files are given in the Supplementary Material.

To convert the DFT magnetic shielding calculated with ADF we use Equation S1 and the parameters found for models C) and D) (see *Reference calculations for DFT chemical shifts*).

Note that, the requirement of full relativistic calculations leads to a drastic increase in computational resources and thus strongly limits the system size and the number of possible local defects which can be evaluated computationally. Also note that the full relativistic calculation of magnetic shielding is currently not available for periodic systems. As a consequence, we perform the chemical shift calculations using a cluster-based approach with ADF. However, for small dopant concentrations the number of atoms required to quantitatively model the defect site typically extends over multiple unit-cells and is thus often prohibitive for full relativistic DFT approaches. Here, we approximate the NMR parameters through computationally accessible limit cases. For the structural hypothesis of defect incorporation, we investigate the limit case of an isolated defect not affecting the perovskite packing (non-relaxed and only Cd or Pb optimized structures) and the limit case of a dense defect area (all atom optimized structures).

Figure S7. Examples of modified clusters extracted for fully relativistic DFT chemical shift calculations. **(A)** $\text{MA}_{18}\text{CdPb}_8\text{I}_{36}$ cluster, **(B)** $\text{MA}_9\text{Pb}_6\text{CdI}_{22}$ cluster, **(C)** $\text{MA}_{24}\text{Cd}_{11}\text{PbI}_{36}$ cluster, **(D)** $\text{Cs}_{18}\text{CdPb}_8\text{Br}_{36}$ cluster, **(E)** $\text{Cs}_8\text{Pb}_{22}\text{Cd}_5\text{Br}_{62}$ cluster, **(F)** $\text{Cs}_8\text{Pb}_{25}\text{Cd}_2\text{Br}_{62}$ cluster with Cd – Cd at 2nd coordination shell, and **(G)** $\text{Cs}_8\text{Pb}_{25}\text{Cd}_2\text{Br}_{62}$ cluster with Cd – Cd at 4th coordination shell. The atoms are colored as follows: hydrogen (white), carbon (brown), nitrogen (blue), cesium (green), lead (gray), cadmium (pink) and iodine (purple). The clusters are not terminated with protons.

Table S7. DFT calculated magnetic shielding and chemical shifts for the investigated clusters of the MAPbI_3 structures doped with ^{113}Cd .

Extracted cluster for ADF calculations	^{113}Cd DFT magnetic shielding (ADF) / ppm	^{113}Cd DFT chemical shifts from reference set C) / ppm	^{113}Cd DFT chemical shifts from reference set D) / ppm
$\text{MA}_{18}\text{CdPb}_8\text{I}_{36}$ Relax ^1H positions in original structure	3597.1	409.6	480.1
$\text{MA}_{18}\text{CdPb}_8\text{I}_{36}$ Relax ^1H positions in original structure Optimize ^{113}Cd position	-654871.3	465130.0	561473.1
$\text{MA}_9\text{Pb}_6\text{CdI}_{22}$ Relax ^1H positions in original structure	2929.8	880.6	1049.2
$\text{MA}_9\text{Pb}_6\text{CdI}_{22}$ Relax ^1H positions in original structure Optimize all atom positions	8869.5	-3311.4	-4011.3

Table S8. DFT calculated magnetic shielding and chemical shifts for the investigated clusters of the CsPbBr₃ structures doped with ¹¹³Cd.

Extracted cluster for ADF calculations	¹¹³ Cd DFT magnetic shielding (ADF) / ppm	¹¹³ Cd DFT chemical shifts from reference set C) / ppm	¹¹³ Cd DFT chemical shifts from reference set D) / ppm
Cs₁₈CdPb₈Br₃₆	-2025406.2	1432397.9	1729121.6
Cs₁₈CdPb₈Br₃₆ <i>Optimize ¹¹³Cd position</i>	-1899322.7	1343413.3	1621702.8
Cs₁₈CdPb₈Br₃₆ <i>Optimize all atom positions</i>	-148084.8	107460.6	129708.4
Cs₈Pb₂₂Cd₅Br₆₂	3980.6	172.9	153.9
Cs₈Pb₂₂Cd₅Br₆₂ <i>Optimize all atom positions</i>	2929.8	880.6	1049.2
Cs₈Pb₂₅Cd₂Br₆₂ Cd – Cd in 2nd coordination shell	4380.3	-143.1	-35.8
Cs₈Pb₂₅Cd₂Br₆₂ Cd – Cd in 4th coordination shell	4228.2	-186.6	-57.0

Table S9. DFT calculated magnetic shielding and chemical shifts for the investigated clusters of the MA₂CdI₄ structures doped with ²⁰⁷Pb.

Extracted cluster for ADF calculations	¹¹³ Cd DFT magnetic shielding (ADF) / ppm	¹¹³ Cd DFT chemical shifts from reference set C) / ppm	¹¹³ Cd DFT chemical shifts from reference set D) / ppm
MA₂₄Cd₁₁PbI₄₈ <i>Relax ¹H positions in original structure</i>	3918.7	182.7	206.6
MA₂₄Cd₁₁PbI₄₈ <i>Relax ¹H positions in original structure</i> <i>Optimize ²⁰⁷Pb position</i>	4066.92	78.0	80.4
MA₂₄Cd₁₁PbI₄₈ <i>Optimize all atom positions</i>	3864.8	220.7	252.6

Cd-doped MAPbI₃

For Cd-doped MAPbI₃ (Table S7), we observe that the all-atom optimized structures lead to unrealistic ¹¹³Cd chemical shifts, indicating that these clusters are not physically reasonable.

The non-relaxed structures lead to ¹¹³Cd chemical shifts in the range of 400-500 ppm (aliovalent Cd²⁺-for-MA substitution) and in the range of 850-1050 ppm (homovalent Cd²⁺-for-Pb²⁺). However, none of these shifts is observed experimentally and the only cadmium-containing species is the non-perovskite MA₂CdI₄ phase.

Cd-doped CsPbBr₃

For Cd-doped CsPbBr₃ (Table S8), we observe that the aliovalent Cs⁺→Cd²⁺ substituted structures all yield unrealistic ¹¹³Cd chemical shifts, indicating that this doping mechanism does not occur.

For the non-relaxed homovalent Cd²⁺-for-Pb²⁺ substituted structure, we observe a ¹¹³Cd chemical shift around 150 ppm. However, we note that the investigated cluster contains four cadmium ions in the 4th coordination shell. This corresponds to clustering at very high dopant ratios.

We thus investigate two further Cd²⁺-for-Pb²⁺ substituted structures with lower cadmium content. Both additional clusters are generated with exactly two cadmium atoms, one with a Cd – Cd in the 2nd coordination shell and one with a Cd – Cd in the 4th coordination shell (see Figure S7, panels F and G). For these two structures, we observe a ¹¹³Cd chemical shift in the range of -30 to -190 ppm. This chemical shift range matches perfectly the experimentally observed broad signal (-110 ppm, fwhm 135 ppm) of a new octahedral [CdBr₆]⁴⁻ species (see Figure 3j).

Pb-doped MA₂CdI₄

For the hypothetical case of Pb-doped MA₂CdI₄, we observe ¹¹³Cd chemical shifts in the range of 80–250 ppm (Table S9) for both the non-relaxed and the all-atom optimized structures. However, the absence of structural disorder in the experimental ¹¹³Cd data excludes the possibility of homovalent Cd²⁺-for-Pb²⁺ doping in MA₂CdI₄.

The probability of finding different $[\text{CdBr}_{4-x}\text{I}_x]^{2-}$ coordination environments in mixed-halide $\text{FA}_2\text{CdI}_{4-x}$ phases

Figure S8. The probability of finding different $[\text{CdBr}_{4-x}\text{I}_x]^{2-}$ coordination environments in mixed-halide $\text{FA}_2\text{CdI}_{4-x}$ phases calculated using binomial distribution and corresponding to homogeneous halide mixing.

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