Exploring Multidimensional Lead Halide Perovskites Using Ultra-wideline $^{35/37}\text{Cl}$ NMR Spectroscopy†

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We report a rapid solid-state $^{35/37}\text{Cl}$ NMR strategy for 3D organic–inorganic hybrid and low-dimensional (2D and 0D) all-inorganic lead-based perovskites embracing ultra-wideline acquisition approaches and moderate to ultrahigh magnetic fields. The observed quadrupolar NMR parameters (C_Q and η), supported by GIPAW–DFT computations, revealed distinct features for unique local Cl environments with the variation of the A-site and dimensionality. ^{35}Cl C_Q values display the potential for becoming an informative probe of distinct Cl chemical environments.

Lead halide perovskites (LHPs) are emerging as a new frontier in next-generation energy materials due to their phenomenal optical and electrical properties.^{1–3} These materials are leading in commercial advances for solar cells,⁴ LEDs,^{5,6} lasers,^{7,8} photodetectors,⁹ X-ray detectors,¹⁰ batteries,^{11,12} and photocatalytic applications.¹³ Recently LHPs have reached power conversion efficiencies of 25.5%,¹⁴ surpassing that for the “gold standard” silicon solar cell. The three-dimensional (3D) LHPs are expressed using the general formula APbX_3 [$\text{A} = \text{Cs}^+$, MA^+ (methylammonium), FA^+ (formamidinium); $\text{X} = \text{Cl}^-$, Br^- , I^-], where the A-site cation resides in the cuboctahedral voids of a corner-sharing 3D network of $[\text{PbX}_6]^{4-}$ octahedra.³ The zero-dimensional (0D) and two-dimensional (2D) LHPs are recent entrants on the block, providing enhanced material stability, photoluminescent properties, and charge carrier recombination dynamics compared to their 3D analogues.^{15–18} Low-dimensional cesium-based 0D and 2D LHPs can be described by the general formula Cs_4PbX_6 and CsPb_2X_5 , respectively, where 0D Cs_4PbX_6 consists of isolated $[\text{PbX}_6]^{4-}$ octahedra surrounded by Cs^+ ,¹⁹ and 2D CsPb_2X_5 is found to have layers of face sharing $[\text{PbX}_8]^{6-}$ side-bicapped trigonal prisms with Cs^+ sandwiched between the layers.²⁰ The crystallographic structures of several n -dimensional lead chloride perovskites explored in this study are shown in **Fig. 1**.

Fig. 1 Crystallographic structures of 3D (a) FAPbCl_3 , (b) MAPbCl_3 , (c) CsPbCl_3 , 2D (d) CsPb_2Cl_5 , and 0D (e) Cs_4PbCl_6 .

Though standard characterization tools, such as diffraction techniques, are traditionally used to characterize average long-range structures of LHPs, they often fail to provide insight into local

disorder, vacancies, dynamics and nanodomains.^{21–23} Solid-state nuclear magnetic resonance (NMR) spectroscopy is a robust analytical method to study short- to medium-range structure and ion dynamics in these systems, complementing diffraction-based approaches.^{24–27} Typically, all the constituents of LHPs have sufficiently abundant and NMR-sensitive isotopes,²⁷ which makes them perfect candidates for NMR analyses. Among all NMR-active nuclei in Cs-based LHPs, ¹³³Cs (nuclear spin, $I = 7/2$; “pseudo- $1/2$ ”) and ²⁰⁷Pb ($I = 1/2$) are the most intensely studied because of their relative accessibility compared to more difficult nuclei, and have contributed significantly to understanding phase transitions,^{28,29} chemical exchange reactions,^{30,31} and phase segregation^{32,33} in LHPs. On the other hand, quadrupolar ($I > 1/2$) halide nuclei (Cl, Br, I) are relatively challenging for NMR spectroscopists because of their broad NMR powder patterns arising from their sizeable quadrupolar moments (Q_m).³⁴ The resulting quadrupolar interactions can be uniquely characterized by two NMR parameters; the nuclear quadrupole coupling constant (C_Q) and the asymmetry parameter (η), and are highly sensitive to the medium-range chemical environment and dynamics. Recent halide magnetic resonance studies have demonstrated their utility in probing chemical structure, geometry, and dynamics in these semiconducting solids.^{27,35–37} Amidst the halogen nuclei, ³⁵Cl ($I = 3/2$) has a comparably moderate Q_m (–81.65 mb) with a good natural abundance (75.78%), and is a perfect choice for NMR studies compared to ^{79/81}Br and ¹²⁷I that have much larger quadrupole moments. While, ³⁷Cl ($I = 3/2$, $Q_m = -64.35$ mb) is complimentary to ³⁵Cl, it is more challenging due to its lower gyromagnetic ratio and natural abundance (24.22 %).^{34,38}

In this communication, we identify unique ³⁵Cl (and ³⁷Cl for CsPbCl₃) NMR parameters for leading hybrid/inorganic and multidimensional lead chloride perovskites, and demonstrate that rapid acquisition (30 to 120 minutes) of wideline NMR spectra are practical. We discuss the highly sensitive nature of ³⁵Cl NMR spectroscopy in elucidating the distinct Cl chemical environments in 0D, 2D and 3D perovskites. It is further demonstrated that quantum chemical computations using gauge-including projector augmented waves³⁹ assisted density functional theory (GIPAW-DFT) reasonably predict the unique NMR parameters.

Non-spinning ³⁵Cl NMR spectra of 3D APbCl₃ ($A = \text{Cs}^+$, MA^+ , and FA^+) at 21.1 T are shown in **Fig. 2**, and display second-order quadrupolar-broadened lineshapes due to the distinct two-coordinate linear or near-linear Cl chemical environments present in these materials. The hybrid species MAPbCl₃ was synthesized using two synthetic routes, inverse temperature crystallization (ITC) and mechanochemical synthesis (MCS) (PXRD pattern, **Fig. S1a**, ESI[†]). All other bulk materials were prepared by MCS, and their NMR parameters are discussed here. MAPbCl₃ exists in a cubic ($Pm\bar{3}m$) crystal structure (PXRD pattern, **Fig. S1a**, ESI[†]) where each Cl atom is covalently bonded⁴⁰ with two Pb atoms in a collinear geometry.⁴¹ The NMR spectrum of MAPbCl₃ (ITC) at 7.05 T was acquired using a Hahn-echo pulse⁴² with 13 variable offset cumulative spectra (VOCS)⁴³ steps (7.5 hrs/step) as well as a wide-band, uniform rate, and smooth truncation Carr-Purcell-Meiboom-Gill (WURST-CPMG)^{44,45} pulse with 5 VOCS steps (25 minutes/step) which offered a ~47-fold savings in time (**Fig. S3**, ESI[†]). Spectral simulation of the experimentally determined parameters of MAPbCl₃ (MCS) obtained from the WURST-CPMG spectrum were $C_Q = 16.34$ MHz, $\eta = 0$, and the isotropic chemical shift (δ_{iso}) = 155 ppm. Likewise, the FAPbCl₃ that is isostructural (PXRD pattern, **Fig. S1a**, ESI[†]) with a slightly larger unit cell volume⁴⁶ due to the larger FA cation has experimentally determined parameters of $C_Q = 17.46$ MHz, $\eta = 0$, and $\delta_{iso} = 160$ ppm. The more stable all-inorganic CsPbCl₃ occupies a lower symmetry orthorhombic structure ($Pnma$) (PXRD pattern, **Fig. S1b**, ESI[†]) where the Cl atoms are coordinated to two lead atoms in two different non-collinear geometries (Pb–Cl–Pb bond angles, $\angle$ of ~161° and 169°).⁴⁷ The WURST-CPMG spectrum fails to resolve these two slightly different Cl environments and

the average NMR parameters for the observed ^{35}Cl signal are $C_Q = 15.60$ MHz, $\eta = 0$, and $\delta_{iso} = 155$ ppm. Utilizing a WURST-echo⁴⁵ and quadrupolar-echo^{48,49} experiment improved our resolution abilities where two distinct Cl chemical environments (with similar parameters $\eta = 0$ and $\delta_{iso} = 150$ ppm, and $C_Q = 15.57$ and 15.71 MHz for $\angle \sim 161^\circ$ and 169° , respectively) are resolved (**Fig. 2a**), and further confirmed using a ^{37}Cl quadrupolar-echo experiment (**Fig. S6**, ESI[†]); the assignments were further supported by quantum chemical computations. The results obtained for CsPbCl_3 are comparable with the recent study by Piveteau *et al.* where bulk CsPbCl_3 in a monoclinic structure ($P2_1/m$) was found to have $C_Q = 15.48$ MHz and $\eta = 0$.³⁵ It is apparent from these three materials that all of them contain axially symmetric Cl EFG tensors ($\eta = 0$) and that among them CsPbCl_3 has the smallest C_Q . We note that the formula unit cell volume (V/Z) shrinks from $\text{FAPbCl}_3 > \text{MAPbCl}_3 > \text{CsPbCl}_3$, which may influence the electric field gradient (EFG) about Cl, whereby the associated C_Q decreases (Fig. S2, ESI[†]). The small octahedral tilting associated with the CsPbCl_3 may be responsible for the ~ 1 MHz reduction in C_Q . In addition, the NMR spectra of these 3D perovskites were also recorded at a lower magnetic field of 7.05 T for comparative analysis (Fig. S4, ESI[†]).

Fig. 2 Experimental WURST-CPMG (black) and simulated (blue) non-spinning ^{35}Cl NMR spectra of 3D non-hybrid (b) CsPbCl_3 , and hybrid (c) MAPbCl_3 and (d) FAPbCl_3 , acquired at 21.1 T at room temperature. Asterisks (*) and the dagger (†) denote the presence of PbCl_2 and an unidentified impurity in MAPbCl_3 and FAPbCl_3 , respectively. (a) The WURST-echo (brown) and quadrupolar-echo (red) non-spinning ^{35}Cl NMR spectra of CsPbCl_3 at 21.1 T

showed resolution between two ^{35}Cl sites with slightly different Pb–Cl–Pb bond angles ($\angle$) with similar Pb–Cl bond distance of ~ 2.8 Å, and corresponding simulations of two ^{35}Cl sites with $\angle \sim 161^\circ$ (violet) and 169° (purple) are shown above the overall simulated spectra (blue).

Fig. 3 Experimental (black) and simulated (blue) non-spinning ^{35}Cl NMR spectra of 2D (a) CsPb_2Cl_5 and 0D (b) Cs_4PbCl_6 using the WURST-CPMG pulse sequence, acquired at 7.05 T at room temperature. The individual simulations for two different ^{35}Cl sites in CsPb_2Cl_5 are shown above the simulated spectra in (a) for three-coordinate Cl (^{33}Cl in purple) and four-coordinate Cl (^{44}Cl in violet). Experimental C_Q values for distinct Cl environments with different coordination numbers are shown in (c).

Extending beyond the 3D materials, **Fig. 3** shows the ^{35}Cl NMR spectra acquired at 7.05 T of non-spinning 2D and 0D non-hybrid perovskites, found in tetragonal ($I4/mcm$)⁵⁰ and rhombohedral ($R\bar{3}c$)⁵¹ crystal structures (PXRD pattern, **Fig. S1b**, ESI[†]), respectively. In **Fig. 3a**, resolution between two distinct polyhedral environments around Cl atoms, viz., three-coordinate ClPb_3 (^{33}Cl) trigonal pyramidal and four-coordinate ClPb_4 (^{44}Cl) square planar⁵⁰ are clearly obtained at moderate and ultrahigh fields with assignments supported by GIPAW-DFT computations. The ^{44}Cl in a planar environment was found to have $C_Q = 14.10$ MHz, $\eta = 0$, and $\delta_{iso} = 190$ ppm, while a decrease in the local coordination environment to ^{33}Cl in pyramidal geometry displays NMR parameters of $C_Q = 9.00$ MHz, $\eta = 0.40$ and $\delta_{iso} = 170$ ppm. The 0D Cs_4PbCl_6 perovskite has six-coordinate PbCs_5 polyhedron around the Cl atoms⁵¹ and is found to have the smallest quadrupole coupling constant ($C_Q = 8.50$ MHz) within this family of compounds, with $\eta = 0.20$ and $\delta_{iso} = 150$ ppm. The unique NMR parameters for the perovskites with different dimensions warranted a closer look. A comparison of the NMR spectra recorded at 21.1 and 7.05 T for the low dimensional perovskites is shown in **Fig. S4**, ESI[†].

As demonstrated above, each perovskite type (3D, 2D and 0D) displays a unique set of NMR parameters. Unlike past NMR studies on the B-sites of Pb and Sn^{31,52–55} that depend on unique chemical shifts for these $I = 1/2$ nuclei, the ^{35}Cl chemical shifts are rather crowded within a 40 ppm range, and thus it is difficult to distinguish distinct chemical shift in NMR spectra that span thousands of ppm; it is therefore, impractical to assess for structural cues based on δ_{iso} . However, the ^{35}Cl quadrupolar parameters (C_Q and η) are distinct for each type of perovskite indicating that the unique EFG for each Cl site may be used to elucidate its unique polyhedral structure. To gain further understanding, a series of quantum chemical computations using GIPAW-DFT were performed to assess the effectiveness of computing ^{35}Cl NMR parameters in perovskites (**Table 1**). **Fig. S7a** and **S7c** (ESI[†]) shows that there is good agreement for the computed $|C_Q|$ and δ_{iso} values when compared with experiment, lending further support that both experimental and theoretical NMR calculations can assist in understanding the changes in Cl structure while also being a helpful tool in predicting nuclear quadrupolar resonance spectra. Surprisingly, the computed η values for the two hybrid LHPs (**Fig. S7b**, ESI[†]) deviated from the expected trend. Closer examination of the local Cl environment for each perovskite reveals a series of unique polyhedra, where their local coordination governs the magnitude

of the ^{35}Cl C_Q . **Fig. 3c** shows the general trend observed between Cl coordination number and C_Q for the 3D, 2D and 0D perovskites including CsCl which has a C_Q of zero due to its spherically symmetric Cl environment. The EFG ellipsoid around ^{35}Cl atoms of the perovskite samples are displayed in **Fig. S8** (ESI[†]), where largest principal component of the EFG tensor (V_{zz}) for all Cl atoms is aligned along its Pb–Cl bond except for four-coordinate Cl ($^{[4]}\text{Cl}$) in CsPb_2Cl_5 .

Table 1 Experimental and GIPAW–DFT computed ^{35}Cl NMR parameters of LHPs.

Materials	CN	$C_Q^{a,b}$ (MHz, ± 0.06)		η^b (± 0.02)		δ_{iso}^b (ppm, ± 15)	
		Expt.	DFT	Expt.	DFT	Expt.	DFT
FAPbCl ₃	2	17.46	–18.47	0.00	0.30	160	134
MAPbCl ₃	2	16.34	–18.24	0.00	0.18	155	140
CsPbCl ₃	2	15.57	–16.52	0.00	0.01	150	194
	2	15.71	–16.92	0.00	0.00	150	120
CsPb ₂ Cl ₅	3	9.00	–8.59	0.40	0.38	170	126
	4	14.10	15.34	0.00	0.00	190	244
Cs ₄ PbCl ₆	6	8.50	–8.92	0.20	0.18	150	142
CsCl (ref.) ^c	8	0.00(1)	0.00	0.00(1)	0.00	114(1)	114

^aSigns of C_Q were not determined experimentally. ^bExperimental errors are mentioned in the header at the top. ^cError representation of reference CsCl is given as, e.g., 114 ± 1 MHz as 114(1) ppm.

In summary, we have demonstrated the utility of $^{35/37}\text{Cl}$ NMR spectroscopy as a fast and sensitive structural probe for exploring unique Cl coordination geometries in Cs-containing n -dimensional ($n = 0, 2$, and 3) perovskites. Distinct EFG tensors for ^{35}Cl sites in these LHPs have exhibited a sizeable range of C_Q values between 8 to 18 MHz, which have recently been shown to extend to over 40 MHz for other Cl-containing systems.^{36,56–60} We highlight that the range of chemical shifts of 40 ppm is very small with respect to the experimental spectral span of thousands of ppm found in these materials, thereby making C_Q much more efficient than δ_{iso} in discriminating specific Cl-centred polyhedral environments. Specifically, C_Q shows a general decreasing trend with an increase in Cl coordination number. Moreover, the reliability of GIPAW–DFT assisted *in silico* analysis in predicting the NMR parameters of Cl-containing lead halide perovskites is helpful in estimating their quadrupolar parameters, which assist in optimizing experimental wideline acquisition parameters as well as predicting quadrupolar frequencies.

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Conflicts of interest

There are no conflicts to declare.

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Materials and Methods

Experimental

All starting materials were purchased from commercial sources and used without further purification: Cesium chloride (CsCl, 99%), and methylamine hydrochloride (MAH, 98%) from Sigma Aldrich (St. Louis, MO, USA); formamidinium hydrochloride (FACl, 97%) from Sigma Aldrich (Oakville, ON, Canada); lead(II) chloride (PbCl₂, 99%) from ACROS Organics (Morris Plains, NJ, USA).

Synthesis

a. Ball-milling synthesis of MAPbCl₃

MAH (1.5 mmol, 101 mg) and PbCl₂ (1.5 mmol, 417 mg) were mixed in 1 : 1 molar ratio, and ground together in an agate mortar for 2–3 minutes. The mixture was transferred to a 50-mL zirconia grinding jar equipped with ~50 g of zirconia balls (diameters of 3, 5, and 8 mm) and sealed. An electric planetary ball mill instrument (Changsha Deco-PBM-V-0.4L) was used for ball-milling of the mixture for 15 minutes at 750 rpm under ambient laboratory conditions, and a clean spatula was used to scrape the inner wall of the jar. The procedure was repeated four times for a total grinding time of 60 minutes to obtain the MAPbCl₃.

b. Ball-milling synthesis of FAPbCl₃

Because of the excessively hygroscopic nature of FACl, an argon-filled glove box was used for mixing of FACl (1 mmol, 81 mg) and PbCl₂ (1 mmol, 278 mg) in 1 : 1 molar ratio, and ground in an agate mortar for 2–3 minutes. The mixture was transferred to a 50-mL vacuum/inert gas stainless-steel lined zirconia grinding jar equipped with ~90 g of zirconia balls (with diameters of 3, 5, and 8 mm) and sealed within the glove box. The sample was taken out of the glove box and ball-milled for 60 minutes at 750 rpm using an electric planetary ball mill instrument (Changsha Deco-PBM-V-0.4L) under ambient laboratory conditions. The grinding jar was then opened inside a glove box, and the sample was removed by scraping the inner wall of the jar using a clean spatula. The procedure was repeated two times for a total grinding time of 120 minutes to obtain the FAPbCl₃.

c. Synthesis of other perovskites

All the other discussed lead halide perovskites were synthesized in previous studies. The detailed procedure for the mechanochemical synthesis of 3D CsPbCl₃, 2D CsPb₂Cl₅ and 0D Cs₄PbCl₆ can be found in the study by Karmakar *et al.*¹ MAPbCl₃ was also synthesized by the inverse temperature crystallization (ITC) technique as discussed in another previous study by Karmakar *et al.*²

Powder X-ray Diffraction (XRD)

The powder XRD measurements were performed under ambient laboratory conditions on a Bruker D8 AVANCE diffractometer (40 kV, 20 mA) system (Department of Chemistry, University of Alberta) equipped with an SSD160 detector and Cu K α radiation source (Cu-K α_1 (λ = 1.5406 Å) and K α_2 (λ = 1.5444 Å) radiation). A zero diffraction Si crystal plate (24.6 mm diameter x 1.0 mm thickness) was used for placing the samples and obtaining the 2 θ scans between 5° to 90° with a step increment of 0.0197°.

Solid-state ^{35}Cl Nuclear Magnetic Resonance (NMR) Spectroscopy

a. 7.05 T NMR Data

NMR data at 7.05 T were acquired at room temperature under non-spinning conditions for samples packed in 4 mm ZrO_2 rotors on a Bruker AVANCE NEO 300 NMR spectrometer. The frequency-stepped wide-band, uniform, and smooth truncation Carr–Purcell–Meiboom–Gill (WURST–CPMG)^{3,4} pulse sequence was used to record the ^{35}Cl NMR spectra for all the samples using a 4 mm double resonance H/X Bruker probe. The variable offset cumulative spectrum (VOCS) technique⁵ was used to acquire the ^{35}Cl NMR sub-spectra with different frequency offsets with step size of 250 kHz; these spectra were added to obtaining the complete spectra. Each sub-spectrum was acquired using the following common experimental parameters: number of echoes = 50, spikelet spacing = 5 kHz, and WURST excitation spectral width = 1 MHz. Other parameters used for all the samples are summarized in **Table S1**.

Table S1. Non-spinning ^{35}Cl NMR experimental parameters used in VOCS employing the WURST–CPMG pulse sequence at 7.05 T. All the samples were prepared by mechanochemical synthesis unless mentioned.

Samples	Recycle Delays (s)	# of Scans	# of Sub-spectra	Total Acquisition Time (Hours)
FAPbCl ₃	0.2	5,120	6	2.0
MAPbCl ₃	0.2	5,120	6	2.0
MAPbCl ₃ (ITC synthesized)	0.1	10,000	5	1.9
CsPbCl ₃	0.5	10,000	5	7.5
CsPb ₂ Cl ₅	1.5	10,000	6	25.6
Cs ₄ PbCl ₆	0.2	10,000	2	1.3

Additionally, a non-spinning ^{35}Cl NMR spectrum of ITC-synthesized MAPbCl₃ was also acquired at room temperature using the same probe by employing Hahn-echo pulse sequence.⁶ A recycle delay of 0.1 s was used, with 13 VOCS steps and a frequency step size of 100 kHz were used to obtain a final spectrum after adding all the sub-spectra. All the ^{35}Cl NMR spectra at 7.05 T were referenced to a secondary standard (solid CsCl, $\delta(^{35}\text{Cl}) = 114$ ppm) with respect to primary standard of 1 M NaCl in H₂O ($\delta(^{35}\text{Cl}) = 0.00$ ppm).

b. 21.1 T NMR Data

Non-spinning ^{35}Cl NMR spectra at 21.1 T were acquired on a Bruker Avance II 900 NMR spectrometer using a home-built 4 mm H/X low-E solenoid probe at room temperature. Samples were packed in 4 mm ZrO_2 Bruker rotors, thin-walled or thick walled depending on the sample volume. WURST–CPMG, WURST–echo,⁴ and quadrupolar–echo^{7,8} pulse sequences were used for all the samples with a primary reference of 1 M KCl in D₂O at $\delta(^{35}\text{Cl}) = 0.00$ ppm; the experimental parameters for the experiments are discussed below.

WURST–CPMG NMR spectra of the mechanochemically synthesized samples were acquired using a WURST excitation spectral width of 2 MHz, 48 echoes, a spikelet spacing of 2 kHz and with proton decoupling when required. Unlike the ^{35}Cl NMR spectra at 7.05 T, the WURST–CPMG NMR spectra at 21.1 T are obtained in a single step reducing the acquisition time significantly.

WURST-echo NMR spectra were obtained using the same WURST pulse parameters discussed above, followed by a single echo acquisition. All other relevant WURST-CPMG and WURST-echo experimental parameters for each of the samples are mentioned in **Table S2**.

Table S2. Non-spinning ^{35}Cl NMR experimental parameters used in WURST-CPMG and WURST-echo pulse sequences at 21.1 T for the mechanochemically synthesized samples. Proton decoupling was used during WURST-CPMG experiment for the samples marked with asterisks (*).

Samples	Recycle Delays (s)	# of Scans		Total Acquisition Time (Hours)	
		WURST-CPMG	WURST-echo	WURST-CPMG	WURST-echo
*FAPbCl ₃	2	1,024	4,096	0.5	2.5
*MAPbCl ₃	2	1,024	4,096	0.5	2.5
CsPbCl ₃	1	4,096	16,384	1.0	4.5
CsPb ₂ Cl ₅	2	1,024	3,072	0.5	1.5
Cs ₄ PbCl ₆	2	1,024	3,072	0.5	1.5

Quadrupolar-echo NMR spectra were obtained by adding different frequency-stepped sub-spectra acquired by employing VOCS technique with a step size of 150 kHz when required. A recycle delay of 1 s and 16,384 scans were used to record the sub-spectra with acquisition time of = 4.5 hrs per step for all the mechanochemically synthesized samples. Quadrupolar-echo NMR spectra of FAPbCl₃ was acquired using five steps with total experimentation time of 22.5 hrs. Similarly, 13.5 hrs were required to obtain the spectra of MAPbCl₃, CsPbCl₃, and CsPb₂Cl₅. The spectrum for Cs₄PbCl₆ was recorded in a single step with an acquisition time of 4.5 hrs.

Solid-state ^{37}Cl NMR Spectroscopy

A non-spinning ^{37}Cl quadrupolar-echo NMR spectrum of CsPbCl₃ was also acquired at 21.1 T on a Bruker Avance II 900 NMR spectrometer using a home-built 4 mm H/X low-E solenoid probe at room temperature. ~50 mg of CsPbCl₃ was packed in a thick-walled 4 mm ZrO₂ Bruker rotor. Three sub-spectra were acquired with frequency stepping of 125 kHz to obtain the complete quadrupolar-echo spectrum using a recycle delay of 1 s, 65,536 co-added transients, and a total acquisition time of 18 hrs.

NMR Data Processing and Analysis

NMR spectra were processed using the Topspin 4.1.1 Bruker software and plotted using the OriginPro 8.5 software. All the $^{35/37}\text{Cl}$ NMR spectra were fit using the WSolids1 NMR simulation package.⁹ Euler angles of the samples were extracted using EFGShield (Version 4.6) to aid in simulation.¹⁰ EFG ellipsoids were visualized using MagresView V 1.6.2.¹¹

Quantum Chemical Computations

The CAMbridge Serial Total Energy Package (CASTEP) software package^{12,13} with NMR modules^{14,15} were used to perform quantum chemical calculations to compute theoretical NMR interaction parameters. The theoretical calculations incorporated tools like the gauge-including projector augmented waves (GIPAW) method,¹⁴ the density functional theory (DFT) method with a plane wave

basis set, the Perdew–Burke–Ernzerhof (PBE)¹⁶ functional, pseudopotentials, and zeroth-order regular approximation (ZORA) relativistic effects. The applied Monkhorst–Pack (MP) grid¹⁷ of $p \times q \times r$ k -points and plane wave cut-off energy with extreme basis set precision are given in the **Table S3**.

Table S3. MP grid k -points and plane wave cut-off energy used for GIPAW–DFT calculations for all the samples.

Samples	MP grid ($p \times q \times r$) k -points	Plane Wave Cut-off Energy (eV)
FAPbCl ₃	12 × 12 × 12	750
MAPbCl ₃	12 × 12 × 12	750
CsPbCl ₃	10 × 7 × 10	750
CsPb ₂ Cl ₅	8 × 8 × 4	750
Cs ₄ PbCl ₆	5 × 5 × 4	392
CsCl (ref.)	10 × 10 × 10	750

All unit-cell parameters and atomic coordinates were taken from their corresponding crystal structures as summarised in **Table S4**. Hydrogen atoms were inserted in the MA and FA cations for hybrid MA– and FAPbCl₃ unit cells using the Avogadro software,^{18,19} and geometry optimizations were performed before calculating NMR parameters. The k -point grid dimension parameters ($p \times q \times r$) were increased until the computed values of the magnetic shielding tensor converged to $\Delta\sigma_{\text{computed}} \leq 1$ ppm. Finally, GIPAW–DFT computed ³⁵Cl magnetic shielding tensor values were converted to chemical shifts using the computed values of CsCl as a reference sample with $\delta(\text{ppm}) \approx \sigma_{\text{ref}}(\text{ppm}) - \sigma_{\text{computed}}(\text{ppm})$, where $\sigma_{\text{ref}} = 914.75$ ppm was used to match the $\delta_{\text{iso}} = 114$ ppm value obtained from the experimental ³⁵Cl solid CsCl spectrum at 7.05 T as previously mentioned.

Table S4. Crystal system, space group and cell parameters of the samples used for GIPAW–DFT calculations.

Samples	Crystal System & Space Group	Cell Parameters						Ref.
		a (Å)	b (Å)	c (Å)	α (deg.)	β (deg.)	γ (deg.)	
FAPCl ₃	Cubic ($Pm\bar{3}m$)	5.74	5.74	5.74	90	90	90	[20]
MAPbCl ₃	Cubic ($Pm\bar{3}m$)	5.69	5.69	5.69	90	90	90	[21]
CsPbCl ₃	Orthorhombic ($Pnma$)	5.59	5.59	5.48	90	90	90	[22]
CsPb ₂ Cl ₅	Tetragonal ($I4/mcm$)	8.27	8.27	15.33	90	90	90	[23]
Cs ₄ PbCl ₆	Rhombohedral ($R\bar{3}c$)	13.18	13.18	16.64	90	90	120	[24]
CsCl (ref.)	Cubic ($Pm\bar{3}m$)	4.11	4.11	4.11	90	90	90	[25]

NMR Parameter Definitions

Detailed discussion about several solid-state NMR interactions and parameters can be found elsewhere.^{26,27} Here, the relevant NMR parameters mentioned in this study are briefly discussed below:

a. Isotropic chemical shift (δ_{iso})

δ_{iso} is the result of averaging the principal components of the anisotropic shift tensor. Chemical shift values (δ) are obtained by converting the magnetic shielding values (σ) in reference to a standard with a specified chemical shift.

In the principal axis frame, the magnetic shielding tensor can be represented as:

$$\sigma = \begin{pmatrix} \sigma_{11} & 0 & 0 \\ 0 & \sigma_{22} & 0 \\ 0 & 0 & \sigma_{33} \end{pmatrix}$$

The diagonal components of the magnetic shielding tensor can be converted to chemical shift values using the following relation:

$$\delta_{ii} = \frac{\sigma_{ref} - \sigma_{ii}}{1 - \sigma_{ref}} \approx (\sigma_{ref} - \sigma_{ii}), i = 1, 2, 3$$

where, the magnetic shielding of $^{35/37}\text{Cl}$ reference, σ_{ref} is considered to be $\ll 1$ to obtain the simplified equation for chemical shift values (δ_{ii}), and the isotropic chemical shift is given by the following equation:

$$\delta_{iso} = \frac{\delta_{11} + \delta_{22} + \delta_{33}}{3}$$

b. Quadrupole coupling constant (C_Q)

Nuclei with nuclear spin, $I > 1/2$ are quadrupolar and have a nuclear quadrupolar moment (Q_m). This Q_m couples with the electric field gradient (EFG) generated by the electric field produced by the electronic charge distribution of its surrounding chemical environment, giving rise to the quadrupolar interaction (QI). The strength of the QI can be understood by the quadrupole coupling constant (C_Q) value, which has a direct relation to the largest principal component of the EFG tensor at the nucleus (V_{zz}) and Q_m , and is defined by the equation:

$$C_Q = \frac{eQ_m V_{zz}}{h}$$

where e = charge of the electron, and h = Planck's constant.

c. Asymmetry parameter (η)

The deviation of the EFG from axial symmetry can be obtained from the asymmetry parameter, η , given by the equation:

$$\eta = \frac{V_{xx} - V_{yy}}{V_{zz}}, (0 \leq \eta \leq 1)$$

where three principal components of EFG tensor follow the trend $|V_{xx}| \leq |V_{yy}| \leq |V_{zz}|$.

Powder XRD Data

Figure S1. Room-temperature powder XRD patterns of (a) hybrid 3D FAPbCl₃ and MAPbCl₃, and (b) 3D CsPbCl₃, 2D CsPb₂Cl₅, and 0D Cs₄PbCl₆. All the samples were prepared by mechanochemical synthesis unless mentioned [MAPbCl₃ (ITC) in (a) was synthesized by the inverse temperature crystallization (ITC) technique]. FAPbCl₃ has an unidentified impurity, denoted by the dagger (†) in (a). The asterisks (*) indicate the presence of PbCl₂ as starting material in mechanochemically synthesized MAPbCl₃ in (a). CsCl was assigned as the impurity in Cs₄PbCl₆ in a previous study by Karmakar *et al.*¹ and is denoted by black circle (●) in (b).

A-site Variation of 3D Perovskites Data

Figure S2. The dependence of experimental (WURST-CPMG) ³⁵Cl C_Q on the formula unit cell volume (V/Z) with A-site variation for 3D lead chloride perovskites.

Solid-state ^{35}Cl NMR Spectroscopy Data

Figure S3. Non-spinning ^{35}Cl WURST-CPMG (black), and Hahn-echo (red) NMR spectra of ITC synthesized MAPbCl_3 acquired at 7.05 T and 293 K. The simulated spectrum is shown at the top (blue) which yielded NMR parameters of $C_Q = 16.34 \pm 0.05$ MHz, $\eta = 0.00 \pm 0.02$, and $\delta_{iso} = 150 \pm 125$ ppm. The signals denoted by the black diamond suit (♦) arise from an unidentified source.

Figure S4. Non-spinning ^{35}Cl WURST-CPMG experimental (black) and simulated (blue) NMR spectra acquired at 21.1 T (top) and 7.05 T (bottom) for mechanochemically synthesized (a) FAPbCl_3 , (b) MAPbCl_3 , (c) CsPbCl_3 , (d) CsPb_2Cl_5 , and (e) Cs_4PbCl_6 . The individual simulations of two different ^{35}Cl sites, three-coordinated Cl (^{35}Cl in purple) and four-coordinated Cl (^{35}Cl in violet) in CsPb_2Cl_5 are shown above the simulated spectra in (d) for both magnetic fields. The signals denoted by the dagger ($\dagger$), asterisks ($*$), and black circle ($\bullet$) in (a), (b), and (e), respectively, correspond to the impurities discussed in the caption to **Figure S1**.

Figure S5. Non-spinning ^{35}Cl WURST-CPMG (black), WURST-echo (red), quadrupolar-echo (royal blue) NMR spectra and their corresponding simulated (blue) spectra at 21.1 T for mechanochemically synthesized (a) FAPbCl₃, (b) MAPbCl₃, (c) CsPbCl₃, (d) CsPb₂Cl₅, and (e) Cs₄PbCl₆. Though resolution between two ^{35}Cl sites with slightly different Pb-Cl-Pb bond angles ($\angle$) in CsPbCl₃ was not clear in WURST-CPMG spectrum, it was obtained in WURST-echo and quadrupolar-echo spectra, and individual simulations of $\angle \sim 161^\circ$ (violet) and 169° (purple) are shown in (c). CsPb₂Cl₅ also displayed resolution between two different ^{35}Cl sites, and three-coordinated Cl (^{35}Cl in purple) and four-coordinated Cl (^{41}Cl in violet) are shown by individual simulations in (d). The impurities discussed in **Figure S1** gave rise to the signals denoted by the dagger (†), asterisks (*), and black circle (●) in (a), (b), and (e), respectively.

Solid-state ^{37}Cl NMR Spectroscopy Data

Figure S6. Non-spinning ^{37}Cl quadrupolar-echo (black) and simulated (blue) NMR spectra of CsPbCl_3 acquired at 21.1 T. The individual simulations of two different ^{37}Cl sites with different Pb–Cl–Pb bond angles ($\angle$) revealed the following NMR parameters: $\angle \sim 161^\circ$ (simulation in purple), and 169° (simulation in violet) displayed $C_Q = 12.27 \pm 0.05$ MHz, and 12.38 ± 0.03 MHz, respectively; both ^{37}Cl sites are axially symmetric with $\eta = 0.00 \pm 0.02$, and $\delta_{\text{iso}} = 150 \pm 10$ ppm.

Quantum Chemical Computational Data

Figure S7. Comparison of the experimental with GIPAW–DFT computed ^{35}Cl (a) C_Q , (b) η , and (c) δ_{iso} for the lead chloride perovskites listed in **Table 1**.

GIPAW–DFT computed ^{35}Cl magnetic shielding tensor values of the secondary reference CsCl were $\sigma_{11} = \sigma_{22} = \sigma_{33} = 800.75$ ppm. Using the relation, $\delta(\text{ppm}) \approx (\sigma_{\text{ref}} - \sigma_{\text{computed}})$ ppm = $(\sigma_{\text{ref}} - 800.75)$ ppm, and $\delta_{\text{iso}} = 114$ ppm found from the experimental ^{35}Cl solid CsCl spectrum at 7.05 T as discussed before, the σ_{ref} value was found to be 914.75 ppm (*i.e.*, $\sigma_{\text{ref}} = \delta + \sigma_{\text{computed}}$ in ppm). This value was used to obtain the calculated the δ_{iso} values for all the samples using the following equations: $\delta_{ii}(\text{ppm}) = (914.75 - \sigma_{ii,\text{computed}})$ ppm, where $i = 1, 2, 3$, and $\delta_{\text{iso}} = (\delta_{11} + \delta_{22} + \delta_{33})/3$.

Table S5. GIPAW–DFT computed ^{35}Cl NMR parameters for FAPbCl₃.

Cl Atoms	Magnetic Shielding Tensor (ppm)			δ_{iso} (ppm)	C_Q (MHz)	η	EFG Tensor			
							V_{ZZ} (au)	Euler Angles (Degree)		
	σ_{11}	σ_{22}	σ_{33}					α	β	γ
Cl(1)	723.95	739.66	945.94	112	−18.89	0.42	0.98	90	0	0
Cl(2)	640.17	670.70	909.10	175	−21.29	0.35	1.11	90	0	0
Cl(3)	739.53	754.85	902.03	116	−15.23	0.14	0.79	90	0	0

Note. Three different Cl atoms along the coordinate axes arises after the hydrogen insertion in the organic FA cation. Average values of C_Q , η and δ_{iso} are listed in **Table 1** for the single ^{35}Cl site of FAPbCl₃.

Table S6. GIPAW–DFT computed ^{35}Cl NMR parameters for MAPbCl₃.

Cl Atoms	Magnetic Shielding Tensor (ppm)			δ_{iso} (ppm)	C_Q (MHz)	η	EFG Tensor			
							V_{ZZ} (au)	Euler Angles (Degree)		
	σ_{11}	σ_{22}	σ_{33}					α	β	γ
Cl(1)	678.70	709.71	932.92	141	−18.90	0.16	0.99	316.49	1.87	70.03
Cl(2)	690.37	721.03	944.47	129	−18.61	0.09	0.97	141.69	1.80	298.63
Cl(3)	686.68	697.72	912.38	149	−17.20	0.29	0.90	223.08	3.77	253.93

Note. Three different Cl atoms along the coordinate axes arises after the hydrogen insertion in the organic MA cation. Average values of C_Q , η and δ_{iso} are listed in **Table 1** for the single ^{35}Cl site of MAPbCl₃.

Table S7. GIPAW–DFT computed ^{35}Cl NMR parameters for CsPbCl₃.

Cl Atoms	Magnetic Shielding Tensor (ppm)			δ_{iso} (ppm)	C_Q (MHz)	η	EFG Tensor			
							V_{ZZ} (au)	Euler Angles (Degree)		
	σ_{11}	σ_{22}	σ_{33}					α	β	γ
Cl(1)	719.74	745.10	903.21	126	−16.52	0.01	0.86	359.54	0.17	267.84
Cl(2)	719.74	745.10	903.21	126	−16.52	0.01	0.86	0.46	0.17	92.16
Cl(3)	719.74	745.10	903.21	126	−16.52	0.01	0.86	179.54	0.17	267.84
Cl(4)	719.74	745.10	903.21	126	−16.52	0.01	0.86	180.46	0.17	92.16
Cl(5)	719.74	745.10	903.21	126	−16.52	0.01	0.86	359.54	0.17	267.84
Cl(6)	719.74	745.10	903.21	126	−16.52	0.01	0.86	0.46	0.17	92.16

Cl(7)	719.74	745.10	903.21	126	−16.52	0.01	0.86	179.54	0.17	267.84
Cl(8)	719.74	745.10	903.21	126	−16.52	0.01	0.86	180.46	0.17	92.16
Cl(9)	730.59	736.12	918.42	120	−16.92	0	0.88	84.81	0	0
Cl(10)	730.59	736.12	918.42	120	−16.92	0	0.88	95.19	0	0
Cl(11)	730.59	736.12	918.42	120	−16.92	0	0.88	84.81	0	0
Cl(12)	730.59	736.12	918.42	120	−16.92	0	0.88	95.19	0	0

Table S8. GIPAW–DFT computed ^{35}Cl NMR parameters for CsPb_2Cl_5 .

Cl Atoms	Magnetic Shielding Tensor (ppm)			δ_{iso} (ppm)	C_Q (MHz)	η	EFG Tensor			
							V_{zz} (au)	Euler Angles (Degree)		
	σ_{11}	σ_{22}	σ_{33}					α	β	γ
Cl(1)	743.66	741.47	688.22	190	−8.59	0.38	0.45	0	18.85	0
Cl(2)	692.69	692.69	626.95	244	15.34	0	0.80	90	90	180
Cl(3)	743.66	741.47	688.22	190	−8.59	0.38	0.45	0	18.85	0
Cl(4)	743.66	741.47	688.22	190	−8.59	0.38	0.45	180	18.85	180
Cl(5)	743.66	741.47	688.22	190	−8.59	0.38	0.45	180	18.85	180
Cl(6)	743.66	741.47	688.22	190	−8.59	0.38	0.45	0	18.85	0
Cl(7)	743.66	741.47	688.22	190	−8.59	0.38	0.45	0	18.85	0
Cl(8)	743.66	741.47	688.22	190	−8.59	0.38	0.45	180	18.85	180
Cl(9)	743.66	741.47	688.22	190	−8.59	0.38	0.45	180	18.85	180
Cl(10)	743.66	741.47	688.22	190	−8.59	0.38	0.45	180	18.85	180
Cl(11)	692.69	692.69	626.95	244	15.34	0	0.80	90	90	180
Cl(12)	743.66	741.47	688.22	190	−8.59	0.38	0.45	180	18.85	180
Cl(13)	743.66	741.47	688.22	190	−8.59	0.38	0.45	0	18.85	0
Cl(14)	743.66	741.47	688.22	190	−8.59	0.38	0.45	0	18.85	0
Cl(15)	743.66	741.47	688.22	190	−8.59	0.38	0.45	180	18.85	180
Cl(16)	743.66	741.47	688.22	190	−8.59	0.38	0.45	180	18.85	180
Cl(17)	743.66	741.47	688.22	190	−8.59	0.38	0.45	0	18.85	0
Cl(18)	743.66	741.47	688.22	190	−8.59	0.38	0.45	0	18.85	0
Cl(19)	692.69	692.69	626.95	244	15.34	0	0.80	90	90	180
Cl(20)	692.69	692.69	626.95	244	15.34	0	0.80	90	90	180

Table S9. GIPAW–DFT computed ^{35}Cl NMR parameters for Cs_4PbCl_6 .

Cl Atoms	Magnetic Shielding Tensor (ppm)			δ_{iso} (ppm)	C_Q (MHz)	η	EFG Tensor			
							V_{zz} (au)	Euler Angles (Degree)		
	σ_{11}	σ_{22}	σ_{33}					α	β	γ

CI(1)	725.01	771.33	821.90	142	-8.92	0.18	0.47	65.10	11.64	69.98
CI(2)	725.01	771.33	821.90	142	-8.92	0.18	0.47	65.14	11.45	249.98
CI(3)	725.01	771.33	821.90	142	-8.92	0.18	0.47	245.13	11.64	249.95
CI(4)	725.01	771.33	821.90	142	-8.92	0.18	0.47	245.14	11.45	69.98
CI(5)	725.01	771.33	821.90	142	-8.92	0.18	0.47	65.10	11.64	69.98
CI(6)	725.01	771.33	821.90	142	-8.92	0.18	0.47	294.90	11.64	110.03
CI(7)	725.01	771.33	821.90	142	-8.92	0.18	0.47	114.87	11.64	290.05
CI(8)	725.01	771.33	821.90	142	-8.92	0.18	0.47	245.14	11.45	69.98
CI(9)	725.01	771.33	821.90	142	-8.92	0.18	0.47	245.13	11.64	249.95
CI(10)	725.01	771.33	821.90	142	-8.92	0.18	0.47	65.14	11.45	249.98
CI(11)	725.01	771.33	821.90	142	-8.92	0.18	0.47	114.87	11.64	290.05
CI(12)	725.01	771.33	821.90	142	-8.92	0.18	0.47	294.90	11.64	110.03
CI(13)	725.01	771.33	821.90	142	-8.92	0.18	0.47	65.10	11.64	69.98
CI(14)	725.01	771.33	821.90	142	-8.92	0.18	0.47	65.14	11.45	249.98
CI(15)	725.01	771.33	821.90	142	-8.92	0.18	0.47	245.17	11.45	249.95
CI(16)	725.01	771.33	821.90	142	-8.92	0.18	0.47	245.13	11.64	69.97
CI(17)	725.01	771.33	821.90	142	-8.92	0.18	0.47	65.13	11.64	69.97
CI(18)	725.01	771.33	821.90	142	-8.92	0.18	0.47	294.90	11.64	110.03
CI(19)	725.01	771.33	821.90	142	-8.92	0.18	0.47	114.83	11.45	290.05
CI(20)	725.01	771.33	821.90	142	-8.92	0.18	0.47	245.14	11.45	69.98
CI(21)	725.01	771.33	821.90	142	-8.92	0.18	0.47	245.13	11.64	249.95
CI(22)	725.01	771.33	821.90	142	-8.92	0.18	0.47	65.13	11.64	249.97
CI(23)	725.01	771.33	821.90	142	-8.92	0.18	0.47	114.87	11.64	290.05
CI(24)	725.01	771.33	821.90	142	-8.92	0.18	0.47	294.87	11.64	110.03
CI(25)	725.01	771.33	821.90	142	-8.92	0.18	0.47	65.13	11.64	69.97
CI(26)	725.01	771.33	821.90	142	-8.92	0.18	0.47	65.13	11.64	249.97
CI(27)	725.01	771.33	821.90	142	-8.92	0.18	0.47	245.13	11.64	249.95
CI(28)	725.01	771.33	821.90	142	-8.92	0.18	0.47	245.14	11.45	69.98
CI(29)	725.01	771.33	821.90	142	-8.92	0.18	0.47	65.10	11.64	69.98
CI(30)	725.01	771.33	821.90	142	-8.92	0.18	0.47	294.87	11.64	110.03
CI(31)	725.01	771.33	821.90	142	-8.92	0.18	0.47	114.87	11.64	290.05
CI(32)	725.01	771.33	821.90	142	-8.92	0.18	0.47	245.13	11.64	69.97
CI(33)	725.01	771.33	821.90	142	-8.92	0.18	0.47	245.17	11.45	249.95
CI(34)	725.01	771.33	821.90	142	-8.92	0.18	0.47	65.14	11.45	249.98
CI(35)	725.01	771.33	821.90	142	-8.92	0.18	0.47	114.83	11.45	290.05
CI(36)	725.01	771.33	821.90	142	-8.92	0.18	0.47	294.90	11.64	110.03

Table S10. Experimental and GIPAW–DFT computed fraction of ^{35}Cl sites in the sample with multiple Cl sites.

Samples	CN	Local Cl Environment	% Fraction of ^{35}Cl Sites	
			Experimental	GIPAW–DFT
CsPbCl_3	2	Pb_2 non-collinear (Pb-Cl-Pb bond angle $\sim 161^\circ$)	62	67
	2	Pb_2 non-collinear (Pb-Cl-Pb bond angle $\sim 169^\circ$)	38	33
CsPb_2Cl_5	3	Pb_3 trigonal pyramidal	80	80
	4	Pb_4 square planar	20	20

a) FAPbCl_3

b) MAPbCl_3

c) CsPbCl_3

d) CsPb_2Cl_5

e) Cs_4PbCl_6

Figure S8. The EFG ellipsoid around the ^{35}Cl atoms of (a) FAPbCl_3 , (b) MAPbCl_3 , (c) CsPbCl_3 , (d) CsPb_2Cl_5 , and (e) Cs_4PbCl_6 . Of interest, V_{zz} for all Cl atoms is aligned along its Pb-Cl bond except for four-coordinate Cl (^{4}I) in CsPb_2Cl_5 in (d).

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