Supplementary Information: The Efficacy of Lewis Affinity Scale Metrics to Represent Solvent Interactions with Reagent Salts in All-Inorganic Metal Halide Perovskite Solutions

Oluwaseun Romiluyi^a, Yannick Eatmon^b, Ruihao Ni^c, Barry P. Rand^d, Paulette Clancy^a

^aDepartment of Chemical and Biomolecular Engineering, Johns Hopkins University, Baltimore, MD 21218
 ^b Department of Chemical and Biological Engineering, Princeton University, Princeton, NJ 08544
 ^c Department of Materials Science and Engineering, Johns Hopkins University, Baltimore, MD 21218
 ^d Department of Electrical Engineering and Andlinger Center for Energy and the Environment, Princeton

University, Princeton, NJ 08544

1. Gutmann Donor Number Affinity Scale (DN)

The Gutmann donor number (DN) is a Lewis affinity scale that was developed in the 1970s [1, 2]. It measures the negative enthalpy of interaction between the Lewis acid, antimony pentachloride (SbCl₅), and a Lewis base (here the solvents). This experiment is conducted in a non-reactive and dilute solution of 1,2-dichloroethane at room temperature. The formation of the 1:1 complex formed between a solvent (base), B, and SbCl₅ for the DN is represented in Figure S1. This Figure shows that the DN is determined by the enthalpy difference between Equations (1) and (2). One drawback to this metric is that DN values are not available for an extensive list of possible solvents. Determining the DN for solvents that have yet to be studied would require experimentation to produce that information. DN values are currently only available for oxygen-bases – mainly carbonyl compounds – and a few nitrogen-, carbon-, and halogen- bases [2, 3]. Moreover, the quality of the required calorimetric measurements are said to be unreliable, which has been attributed to the high reactivity and catalytic effect of SbCl₅ and weak bases since the complexation reaction (2) was incorrectly assumed to be complete [1, 4]. Overall, these issues have often discouraged the use of the DN as a measure of Lewis affinity and have elevated the possibility of using a BF₃-based affinity scale as an alternative [4]. DN results are described below.



Figure S1: Equations defining the evaluation of the Gutmann DN (left) and a visual schematic of the complexation reaction (right) from [2] used with author's permission.

2. BF₃ Affinity Scale

The BF_3 affinity scale (BF_3) was introduced in the 1970s [2] and, like the DN, it measures the Lewis affinity of a Lewis base to a Lewis acid, here boron trifluoride

 (BF_3) [1, 2]. Experimental determinations of BF_3 can be conducted in a gas or solvent medium of dichloromethane [2]. Figure S2 presents a schematic of the BF_3 reaction and calculation of the BF_3 metric in a solution phase. One advantage of the BF_3 scale over the DN is the existence of a much larger database of BF_3 values, which have been reported for a broader range of bases [1]. It is also thought not to suffer from the reproducibility issues that tend to limit the DN scale [4]. BF_3 values for the solvents used in this study are provided in the Tables below.



Figure S2: Equations defining the evaluation of the BF_3 -based scale (left) and a visual schematic of the relevant complexation reaction (right) from [2] used with author's permission.

3. Lithium Cation Affinity (LCA)

The gas-phase lithium cation affinity (LCA) was first reported in 1975, demonstrating values for 30 ligands from ion cyclotron resonance (ICR) ligand-exchange equilibrium measurements at room temperature [2]. Experiments to measure LCA in the gas-phase are normally performed using mass spectrometer techniques like ICR and collision-induced dissociation threshold (CIDT) [2]. Other gas-phase cation affinity scales exist, *e.g.*, using sodium, potassium,[5] cesium,[6] aluminium, manganese, cyclopentadienyl, nickel and copper cations instead of lithium. But because there is a wider range of data available for the LCA, we studied this scale over other possible cationic scales. Figure S3 provides a schematic representation of the enthalpic changes governing the LCA scale. Corresponding LCA (at 0 K) values for the solvents used in this study are provided in the Tables below.

Solvent +
$$Li^+ \rightarrow [Solvent - Li^+] + \Delta H_{adduct}$$
 (1)
 $Li^+ + LB \rightleftharpoons LB - Li^+$
 $LCA = -\Delta H_{adduct}$ (2)

Figure S3: The simple equation defining the evaluation of the LCA scale (left) and the corresponding reaction (right).

4. Training and Prediction Results

We report supporting information for the fitting and prediction of the Lewis affinity metrics (DN, BF₃, and LCA) from Equations S1-6. We used *ab initio* density functional theory (DFT) calculations to calculate the change in enthalpy resulting from the formation of a 1:1 adduct of solvents with the Lewis acids of the DN, BF₃, and LCA as shown in Equations S1, S3 and S5. We used the functionals outlined in the main text with a triple zeta basis set (def2-TZVP)[7] to optimize the energetic and structural characteristics of solvent-Lewis acid complexes and their constituents (acid alone and a single solvent molecule of each solvent studied) at 0 K in dielectric media of dicholoethane, dichloromethane and in vacuum for the DN, BF₃ and LCA, respectively, with an energy tolerance of 6.0×10^{-6} kcal/mol. We fit results from each affinity scale to their

corresponding experimental values (at 298 K for the DN and BF_3 and at 0 K for the LCA) derived from various literature sources [2, 8, 9]. The solvents used in this study for the prediction, testing and training of the different scales, as well as the solvents employed for perovskite acid affinity estimations are shown in Table S1 and S2.



Figure S4: Schematic showing the DN, BF₃, and LCA interactions based on their respective reference Lewis acid and base and the resulting adduct.

$$-BE_{DN} = E(Base - SbCl_5) - E(Base) - E(SbCl_5)$$
(S1)

Determination of binding enthalpy of the constituents contributing to the DN (BE_{DN}) i.e. the DFT energies associated with the Base-SbCl₅ adduct E(Base-SbCl₅), along with Base E(Base) and SbCl₅ E(SbCl₅) acid in isolation - all simulated in an implicit solvent medium of 1,2-dicholoroethane (dielectric = 10.6).

$$DN = b_0 + b_1 B E_{DN} \tag{S2}$$

Determination of linear model for DN estimation. For this equation, BE represents the binding enthalpy via the 8 DFT methods studied, b_1 represents the slope and b_0 the intercept.

$$-BE_{BF3} = E(Base - BF_3) - E(Base) - E(BF_3)$$
(S3)

Determination of binding enthalpy of the constituents contributing to the BF_3 scale (BE_{BF3}) i.e. the DFT energies associated with the Base-BF₃ adduct E(Base-BF₃), along with Base E(Base) and BF₃ E(BF₃) acid in isolation - all simulated in an implicit solvent medium of dichloromethane (dielectric = 8.96).

$$BF_3 = b_0 + b_1 BE_{BF3} \tag{S4}$$

Determination of linear model for BF_3 estimation. For this equation, BE represents the binding enthalpy via the 8 DFT methods studied, b_1 represents the slope and b_0 the intercept.

$$-BE_{LCA} = E(Base - Li^{+}) - E(Base) - E(Li^{+})$$
(S5)

Determination of binding enthalpy of the constituents contributing to the DN (BE_{LCA}) i.e. the DFT energies associated with the Base-Li⁺ adduct E(Base-Li⁺), along with Base E(Base) and Li⁺ E(Li⁺) acid in isolation - all simulated in vacuum.

$$LCA = b_0 + b_1 B E_{LCA} \tag{S6}$$

Determination of linear model for LCA estimation. For this equation, BE represents the binding enthalpy via the 8 DFT methods studied, b_1 represents the slope and b_0 the intercept.

$$-BE_{Adduct} = E(Solvent - BX_n/A^+) - E(Solvent) - E(BX_n/A^+)$$
(S7)

Determination of binding enthalpy of the constituents contributing to the adduct formed between the solvent and Lewis acid in perovksite solution (perovskite acid) i.e. the DFT energies associated with the solventperovskite acid adduct $E(Solvent-BX_n/A^+)$, along with solvent E(Solvent) and perovskite acid $E(BX_n/A^+)$ in isolation - all simulated in an implicit solvent medium of the solvent.

$$DFT_{RMSE} (All) = \sqrt{\frac{1}{n} \sum_{i}^{n} \left(E_{i,DFT} - E_{i,EXP} \right)^2}$$
(S8)

Determination of root mean squared error (RMSE) derived from the experimental data of the training and test set $E_{i,EXP}$ and raw-DFT binding enthalpies $E_{i,DFT}$.

$$DFT_{MAE} (All) = \frac{1}{n} \sum_{i}^{n} |E_{i,DFT} - E_{i,EXP}|$$
(S9)

Determination of mean absolute error (MAE) derived from the experimental data of the training and test set $E_{i,EXP}$ and raw-DFT binding enthalpies $E_{i,DFT}$.

$$MOD_{RMSE} (Test) = \sqrt{\frac{1}{n} \sum_{i}^{n} (E_{i,MOD} - E_{i,EXP})^2}$$
(S10)

Determination of root mean squared error (RMSE) derived from the experimental data of the testing set $E_{i,EXP}$ and linear model estimations of the experimental values $E_{i,MOD}$.

$$MOD_{MAE} (Test) = \frac{1}{n} \sum_{i}^{n} |E_{i,MOD} - E_{i,EXP}|$$
(S11)

Determination of mean absolute error (MAE) derived from the experimental data of the testing set $E_{i,EXP}$ and linear model estimations of the experimental values $E_{i,MOD}$.

Solvent	Acronym	DN	BF ₃	LCA	Perovskites
Acetonitrile	ACN	\checkmark	\checkmark	\checkmark	✓
Propylene carbonate	PC	\checkmark	\checkmark	\checkmark	1
Etylene carbonate	EC	\checkmark	\checkmark	\checkmark	\checkmark
Butyronitrile	N/a	\checkmark	\checkmark	X	X
Acetone	ACE	\checkmark	\checkmark	\checkmark	\checkmark
Butanone	N/a	\checkmark	\checkmark	X	X
Gamma-butyrolactone	GBL	\checkmark	\checkmark	1	1
Tetrahydrofuran	THF	\checkmark	\checkmark	\checkmark	\checkmark
Trimethyl phosphate	TMP	\checkmark	\checkmark	X	X
Dimethylformamide	DMF	\checkmark	\checkmark	1	\checkmark
N-methyl-pyridinone	NMP	\checkmark	\checkmark	\checkmark	\checkmark
Dimethylacetamide	DMAC	\checkmark	\checkmark	\checkmark	\checkmark
Dimethyl sulfoxide	DMSO	\checkmark	1	✓	1
Dimethyl propylene urea	DMPU	\checkmark	1	✓	1
Pyridine	N/a	\checkmark	\checkmark	1	1
Hexamethylphosphoamide	HMPA	\checkmark	1	1	1
Dibutyl sulfoxide	DBSO	\checkmark	1	X	X
1,3-Dimethyl-2-imidazolidinone	DMI	\checkmark	1	1	1
Diethyl carbonate	N/a	\checkmark	1	X	X
Diethyl ether	DE	\checkmark	1	1	1
Ethyl acetate	N/a	\checkmark	\checkmark	X	X
Diethylformamide	DEF	\checkmark	1	1	1
Propionitrile	N/a	\checkmark	1	1	1
Formamide	N/a	1	1	1	1
Ethanol	N/a	X	X	1	X
Water	N/a	X	X	1	X
Dimethyl ether	N/a	X	X	1	X
Acetaldehyde	N/a	X	X	1	X
2-Aminepyridine	N/a	X	X	1	×
2-Propanol	N/a	X	X	1	×
2-Butanol	N/a	X	X	1	X
2-Methyl-1-propanol	N/a	X	X	1	X
Propylamine	N/a	X	X	1	X
Ammonia	N/a	X	X	1	X
Imidazole	N/a	X	X	1	X
Glvcine	N/a	X	X	1	X
1.2 - Dimethoxyethane	N/a	x	X	✓	X
2-Methylpyridine	N/a	X	X	✓	X
Methanol	N/a	x	x		X

Table S1: Solvents studied with their acronyms and the scales for which they were calculated (DN, BF₃, LCA, and perovskite systems). In this Table, \checkmark indicates the solvents were used (or predicted) here for that particular scale while \varkappa indicates that they were not.

Solvent	Acronym	DN	BF ₃	LCA	Perovskites
1-Propanol	N/a	X	X	1	X
Pyrazole	N/a	X	X	\checkmark	X
Carbon monoxide	CO	X	X	1	×
t-Butanol	N/a	X	X	1	X
3-Aminopyridine	N/a	X	X	\checkmark	X
3-Methylpyridine	N/a	X	X	1	X
Diethyl sulfoxide	DESO	\checkmark	\checkmark	\checkmark	\checkmark
N-methylpyrrolidine-2-thione	NMPT	\checkmark	\checkmark	1	\checkmark
Dimethylthioformamide	DMTF	\checkmark	\checkmark	\checkmark	\checkmark
Tetrahydrothiophene-1-oxide	THTO	\checkmark	\checkmark	1	\checkmark
Phospharamide	PA	\checkmark	\checkmark	1	×
Urea	N/a	\checkmark	\checkmark	\checkmark	X
Thiourea	N/a	\checkmark	\checkmark	1	\checkmark
1,3-Dimethyl -1,3-diazinnae-2-thione	DMDT	\checkmark	\checkmark	1	X
Methylamine	MA	\checkmark	\checkmark	\checkmark	\checkmark

Table S2: Solvents studied with their acronyms and the scales for which they were calculated (DN, BF₃, LCA, and perovskite systems). In this Table, \checkmark indicates the solvents were used (or predicted) here for that particular scale while \checkmark indicates that they were not. Continued from Table S1.

Table S3: Accuracy determined for predicted Gutmann donor number values in terms of R^2 and other error metrics for eight different DFT functionals (-D indicating that a dispersion correction was included with the functional method) and equations describing linear models (x in the equation represents the binding enthalpy (BE)).

DFT Functional	Linear model (R ²)	DFT _{RMSE(MAE)}	MOD _{RMSE(MAE)}	4-fold CV (\mathbb{R}^2)
B97	1.28x + 3.6 (0.92)	8.3 (7.9)	2.8 (2.0)	0.85
PW6B95	1.13x + 1.2 (0.92)	4.4 (3.8)	2.3 (1.8)	0.88
PBE	1.26x + 1.5 (0.91)	6.6 (6.0)	2.7 (2.0)	0.82
B3LYP	1.25x + 4.7 (0.92)	8.9 (8.5)	3.6 (2.4)	0.85
B97-D	1.02x + 0.7 (0.97)	1.8 (1.5)	1.6 (1.4)	0.94
PW6B95-D	0.97x + 0.3 (0.98)	1.5 (1.2)	1.8 (1.7)	0.95
PBE-D	1.13x - 1.0 (0.96)	2.5 (2.0)	1.9 (1.6)	0.93
B3LYP-D	1.01x + 0.9 (0.97)	1.9 (1.6)	2.0 (1.9)	0.94

Table S4: Accuracy determined for predicted BF_3 values in terms of R^2 and other error metrics for eight different DFT functionals (-D indicating that a dispersion correction was included with the functional method) and equations describing linear models (x in the equation represents the binding enthalpy (BE)).

DFT Functional	Linear model (R ²)	DFT _{RMSE(MAE)}	MOD _{RMSE(MAE)}	4-fold CV (R ²)
B97	1.00x + 4.8 (0.93)	5.0 (4.8)	1.5 (1.4)	0.89
PW6B95	0.96x + 1.8 (0.95)	1.3 (0.9)	0.7 (0.6)	0.95
PBE	1.03x + 3.0 (0.91)	3.6 (3.3)	1.2 (1.1)	0.90
B3LYP	0.98x + 5.4 (0.89)	5.0 (4.8)	1.2 (1.0)	0.86
B97-D	0.94x + 6.6 (0.92)	5.6 (5.4)	1.3 (1.1)	0.91
PW6B95-D	0.91x + 1.7 (0.95)	1.2 (0.9)	0.8 (0.6)	0.95
PBE-D	0.96x + 2.7 (0.93)	2.1 (1.6)	1.1 (1.0)	0.93
B3LYP-D	0.86x + 4.5 (0.93)	2.2 (1.9)	0.8 (0.6)	0.91

Table S5: Accuracy determined for predicted lithium cation affinity (LCA) values in terms of R^2 and other error metrics for eight different DFT functionals (-D indicating that a dispersion correction was included with the functional method) and equations describing linear models (x in the equation represents the binding enthalpy (BE)).

DFT Functional	Linear model (R ²)	DFT _{RMSE(MAE)}	$MOD_{RMSE(MAE)}$	4-fold CV (R ²)
B97	0.96x+0.8 (0.96)	2.1 (1.8)	0.7 (0.5)	0.93
PW6B95	0.95x+0.4 (0.96)	2.6 (2.3)	0.7 (0.5)	0.94
PBE	0.96x+0.4 (0.96)	2.2 (2.0)	0.9 (0.7)	0.92
B3LYP	0.95x+0.1 (0.96)	2.8 (2.5)	0.5 (0.4)	0.93
B97-D	0.98x-0.2 (0.96)	2.1 (1.7)	0.8 (0.7)	0.94
PW6B95-D	0.94x+0.3 (0.96)	3.2 (2.7)	0.8 (0.6)	0.93
PBE-D	0.88x+4.4 (0.86)	3.6 (2.7)	1.3 (1.2)	0.70
B3LYP-D	0.93x+0.2 (0.96)	3.4 (3.0)	0.5 (0.4)	0.93



Figure S5: Comparison of binding enthalpies estimated using DFT to predicted values of the BF₃ for four DFT models, listed in the inset, which either included (a) or excluded (b) a dispersion correction. Color code as in the inset. Experimental values are shown as a green line which represents the line of equality (y = x) i.e. an ideal DFT method that yields BF₃ values identical to experimental data.



Figure S6: Comparison of binding enthalpies estimated using DFT to predicted values of the LCA for four DFT models, listed in the inset, which either included (a) or excluded (b) a dispersion correction. Color key as in Figure S5. Experimental values are shown as a green line which represents the line of equality (y = x) i.e. an ideal DFT method that yields LCA values identical to experimental data.

Solvent	DN _{EXP}	BE _{<i>B</i>97}	BE _{PW6B95}	BE _{PBE}	BE _{B3LYP}
ACN	14.4	9.4	13.4	11.2	8.6
PC	15.0	9.3	12.5	10.6	8.8
EC	15.0	8.7	12.4	10.4	7.4
Butyronitrile	16.7	9.7	12.2	11.5	8.8
Acetone	18.1	10.9	14.6	13.8	10.3
Butanone	17.3	11.5	15.4	14.5	10.9
GBL	18.0	10.4	14.5	12.5	9.9
THF	20.6	12.7	17.9	14.9	12.5
TMP	23.0	16.0	20.0	15.0	16.0
DMF	26.6	21.3	25.2	22.8	20.9
NMP	27.3	19.4	23.8	21.2	18.8
DMI	27.6	18.2	18.2	20.3	20.1
DMAC	27.8	18.8	23.4	20.8	18.0
DMSO	29.8	22.5	26.8	24.4	22.0
DMPU	33.0	21.1	27.4	22.6	20.4
DBSO	31.0	22.9	28.3	24.8	22.0
Pyridine	33.5	23.3	27.8	26.1	22.2
HMPA	38.8	22.6	29.8	24.8	22.7

Table S6: Binding enthalpy results for the Gutmann donor number (DN) using the training set solvents for four DFT functionals **without dispersion terms**. Results given for 18 solvents. Experimental values for the 18 solvents are shown in the first column.

Table S7: Binding enthalpy results for the Gutmann donor number (DN) using the training set solvents for four DFT functionals **with dispersion terms**. Results given for 18 solvents. Experimental values for the 18 solvents are shown in the first column.

Solvent	DN _{EXP}	BE _{<i>B</i>97}	BE _{PW6B95}	BE _{PBE}	BE _{B3LYP}
ACN	14.4	13.2	14.4	13.4	12.7
PC	15.0	13.6	15.8	14.0	14.2
EC	15.0	12.9	15.3	13.5	13.6
Butyronitrile	16.7	14.2	15.2	14.2	13.5
Acetone	18.1	17.6	18.4	17.2	16.6
Butanone	17.3	18.7	19.3	18.5	18.0
GBL	18.0	16.2	16.9	16.2	16.4
THF	20.6	21.4	22.4	19.7	21.2
TMP	23.0	22.4	22.7	22.4	24.6
DMF	26.6	26.0	28.3	26.0	26.6
NMP	27.3	26.0	27.9	25.5	26.3
DMI	27.6	27.0	28.8	25.9	27.3
DMAC	27.8	25.6	27.8	24.5	26.2
DMSO	29.8	28.8	30.9	27.9	28.3
DMPU	33.0	30.3	33.5	28.7	31.4
DBSO	31.0	31.9	34.4	30.5	31.6
Pyridine	33.5	32.1	33.4	30.5	30.5
HMPA	38.8	35.0	37.8	32.2	35.2

Table S8: Binding enthalpy results for the Gutmann donor number (DN) using the test set solvents for four DFT functionals **without dispersion terms**. Results given for five solvents not used in the training set. Experimental values for the five solvents are shown in the first column.

Solvent	DN_{EXP}	BE_{B97}	BE_{PW6B95}	BE_{PBE}	BE_{B3LYP}
Diothyl carbonata	16.0	11.0	15 /	12 5	11 1
Dietifyi Carbonate	10.0	11.0	15.4	15.5	11.1
Diethyl ether	19.0	8.0	12.0	9.7	5.5
Ethyl acetate	17.1	10.7	14.6	12.8	9.9
DEF	31.0	22.7	26.6	24.4	22.1
Propionitrile	16.1	9.6	12.3	11.3	8.8

Table S9: Binding enthalpy results for the Gutmann donor number (DN) using the test set solvents for four DFT functionals **with dispersion terms**. Results given for five solvents not used in the training set. Experimental values for the five solvents are shown in the first column.

Solvent	DN _{EXP}	BE _{<i>B</i>97}	BE _{PW6B95}	BE _{PBE}	BE _{B3LYP}
Diethyl carbonate	16.0	17.7	19.1	17.7	18.0
Diethyl ether	19.0	17.5	17.4	15.4	15.8
Ethyl acetate	17.1	17.0	18.5	16.9	17.0
DEF	31.0	28.4	30.4	28.3	28.7
Propionitrile	16.1	13.7	14.9	14.0	13.2



Figure S7: Errors in the DFT estimation of the Gutmann donor number derived from all the data.



Figure S8: Errors in the linear model estimation of the Gutmann donor number derived from the testing data.

Table S10: Binding enthalpies for 18 Solvents predicted by the BF ₃ scale using the training set solver	ıts
for four DFT functionals without dispersion terms. Results given for 18 solvents. Experimental valu	les
for the 18 solvents are shown in the first column.	

Solvent	$BF_{3,EXP}$	BE _{<i>B</i>97}	BE _{PW6B95}	BE _{PBE}	BE _{B3LYP}
ACN	14.5	10.7	13.3	13.1	10.5
PC	15.4	11.1	14.5	11.9	11.1
EC	15.9	10.5	14.1	11.7	10.5
Butyronitrile	14.7	11.0	13.6	13.3	10.7
Acetone	18.2	13.7	17.8	15.8	13.7
Butanone	18.3	14.1	18.2	16.2	14.2
GBL	18.0	13.0	17.3	14.3	13.2
THF	21.7	16.8	21.0	18.3	17.4
TMP	20.4	16.0	20.1	16.2	15.1
DMF	26.5	21.6	25.4	23.2	22.0
NMP	27.0	21.9	26.4	23.1	22.1
DMAC	26.9	16.9	21.8	18.4	17.2
DMSO	25.3	20.4	25.4	21.9	20.9
DMPU	27.0	21.5	26.2	22.7	17.5
Pyridine	30.7	26.5	29.9	28.6	26.4
HMPA	28.2	24.3	28.0	24.3	24.4
DBSO	25.8	22.2	26.3	23.0	22.3
DMI	23.7	18.1	22.6	19.4	20.0

Table S11: Binding enthalpies for 18 Solvents predicted by the BF_3 scale using the training set solvents for four DFT functionals **with dispersion terms**. Results given for 18 solvents. Experimental values for the 18 solvents are shown in the first column.

Solvent	$BF_{3,EXP}$	BE _{<i>B</i>97}	BE _{PW6B95}	BE_{PBE}	BE _{B3LYP}
ACN	14.5	9.8	14.0	13.9	11.8
PC	15.4	9.6	15.5	13.6	13.3
EC	15.9	9.3	15.0	13.0	11.4
Butyronitrile	14.7	9.7	14.4	14.3	12.3
Acetone	18.2	13.2	18.9	16.0	16.6
Butanone	18.3	13.8	19.4	18.0	17.3
GBL	18.0	12.4	18.4	16.4	16.1
THF	21.7	17.7	22.4	18.9	21.4
TMP	20.4	13.1	20.0	18.1	21.2
DMF	26.5	19.9	26.3	23.8	24.1
NMP	27.0	20.9	27.6	25.0	25.3
DMAC	26.9	16.6	23.2	20.6	21.1
DMSO	25.3	20.0	26.7	23.4	23.7
DMPU	27.0	21.3	27.9	25.4	26.0
Pyridine	30.7	26.3	31.2	30.6	29.8
HMPA	28.2	24.6	29.9	27.8	29.1
DBSO	25.8	21.5	28.0	25.1	25.5
DMI	23.7	18.0	24.6	21.6	22.2

Table S12: Binding enthalpy results for the BF_3 using the test set solvents for four DFT functionals **without dispersion terms**. Results given for five solvents not used in the training set. Experimental values for the five solvents are shown in the first column.

Solvent	$BF_{3,EXP}$	BE_{B97}	BE _{PW6B95}	BE_{PBE}	BE _{B3LYP}
Diethyl carbonate	17.0	13.8	17.3	15.0	13.9
Diethyl ether	19.0	11.6	18.3	15.0	13.8
Ethyl acetate	18.1	13.7	17.7	15.2	13.7
DEF	27.2	23.2	27.0	24.3	23.5
Propionitrile	14.6	11.0	13.6	13.3	10.7

Table S13: Binding enthalpy results for the BF_3 using the test set solvents for four DFT functionals with dispersion terms. Results given for five solvents not used in the training set. Experimental values for the five solvents are shown in the first column.

Solvent	BF ₃ , _{EXP}	BE _{<i>B</i>97}	BE _{PW6B95}	BE _{PBE}	BE _{B3LYP}
Diethyl carbonate	17.0	12.9	18.4	16.6	16.4
Diethyl ether	19.0	14.9	18.4	17.9	16.9
Ethyl acetate	18.1	13.0	18.8	17.0	16.8
DEF	27.2	21.8	28.0	25.7	26.0
Propionitrile	14.6	10.2	14.3	14.1	12.1



Figure S9: Errors in the DFT estimation of the BF_3 derived from all the data.



Figure S10: Errors in the linear model estimation of the BF_3 derived from the testing data.

Table S14: Binding enthalpies for 18 Solvents predicted by the LCA scale using the training set solvents
for four DFT functionals without dispersion terms. Results given for 18 solvents. Experimental values
for the 18 solvents are shown in the first column.

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Solvent	LCA _{EXP}	BE _{<i>B</i>97}	BE _{PW6B95}	BE_{PBE}	BE _{B3LYP}
Butanone	45.5	47.2	47.4	46.9	48.6
Ethanol	39.1	40.4	41.4	40.6	41.7
Water	31.8	36.1	36.9	36.4	37.0
CO	13.2	11.8	12.5	11.6	12.8
Pyrazole	44.8	43.6	45.5	45.2	46.1
Pyridine	43.3	46.1	46.6	46.4	47.1
Dimethyl ether	39.5	37.9	38.7	37.7	39.3
Acetaldehyde	39.8	42.1	42.9	42.0	43.5
2-Aminopyridine	56.9	54.2	55.1	53.8	55.2
2-Propanol	41.3	41.2	42.0	41.5	42.6
2-Butanol	41.7	43.5	44.7	44.0	44.7
2-Methyl-1-propanol	40.4	42.3	43.7	42.8	43.6
Propylamine	47.3	44.8	45.4	45.5	45.4
Ammonia	38.1	41.1	41.6	41.6	41.7
Imidazole	50.4	52.4	52.7	52.2	53.1
Glycine	52.6	53.0	53.6	53.1	54.0
1,2-Dimethoxyethane	57.7	61.1	63.2	60.7	63.3
2-Methylpyridine	46.5	47.4	47.8	47.8	48.3

Table S15: Binding enthalpies for 18 Solvents predicted by the LCA scale using the training set solvents for four DFT functionals **with dispersion terms**. Results given for 18 solvents. Experimental values for the 18 solvents are shown in the first column.

Solvent	LCA _{EXP}	BE _{<i>B</i>97}	BE _{PW6B95}	BE _{PBE}	BE _{B3LYP}
Butanone	45.5	47.0	48.2	47.3	49.4
Ethanol	39.1	41.0	42.1	40.8	42.1
Water	31.8	35.5	37.1	36.4	37.1
CO	13.2	12.4	12.9	12.5	13.0
Pyrazole	44.8	45.1	46.2	31.9	47.0
Pyridine	43.3	45.8	47.3	46.8	47.8
Dimethyl ether	39.5	38.4	39.4	38.1	40.0
Acetaldehyde	39.8	41.3	43.4	42.2	43.9
2-Aminopyridine	56.9	53.1	55.9	54.2	56.0
2-Propanol	41.3	41.6	42.7	41.9	43.4
2-Butanol	41.7	44.5	45.6	44.4	45.5
2-Methyl-1-propanol	40.4	43.5	44.8	43.2	44.2
Propylamine	47.3	46.2	46.3	45.8	46.0
Ammonia	38.1	40.9	41.9	41.6	41.8
Imidazole	50.4	51.5	53.3	52.6	53.8
Glycine	52.6	52.3	54.1	53.4	54.5
1,2-Dimethoxyethane	57.7	61.6	64.4	61.4	64.5
2-Methylpyridine	46.5	48.1	48.7	48.2	49.1

Table S16: Binding enthalpy results for the LCA using the test set solvents for four DFT functionals **without dispersion terms**. Results given for five solvents not used in the training set. Experimental values for the five solvents are shown in the first column.

Solvent	LCA_{EXP}	BE_{B97}	BE _{PW6B95}	BE _{PBE}	BE _{B3LYP}
Methanol	37.1	37.9	38.7	37.9	39.1
1-Propanol	40.7	42.8	43.7	43.1	43.6
t-Butanol	42.6	43.4	44.6	44.0	44.7
3-Aminopyridine	48.3	50.3	50.7	51.2	51.3
3-Methylpyridine	47.0	48.4	48.3	48.5	48.9

Table S17: Binding enthalpy results for the LCA using the test set solvents for four DFT functionals **with dispersion terms**. Results given for five solvents not used in the training set. Experimental values for the five solvents are shown in the first column.

Solvent	LCA _{EXP}	BE _{<i>B</i>97}	BE _{PW6B95}	BE _{PBE}	BE _{B3LYP}
Methanol	37.1	37.4	39.2	38.1	39.6
1-Propanol	40.7	42.6	44.6	43.3	44.2
t-Butanol	42.6	42.7	45.6	44.5	45.6
3-Aminopyridine	48.3	50.5	51.4	51.6	52.0
3-Methylpyridine	47.0	48.5	49.0	49.0	49.6



Figure S11: Errors in the DFT estimation of the LCA derived from all the data.



Figure S12: Errors in the linear model estimation of the LCA derived from the test data.

5. Exploring Perovskite Lewis Acids

The solvents and perovskite solution species explored in this study are listed in Table S18. We extended the binding enthalpy calculations shown in Equation S1, S3, and S5 to the adducts formed between solvents and B-cation salt complexes and A-cation species in all-inorganic perovskite solutions shown in Equation S7. This includes BX₂ salts (PbX₂, SnX₂, and GeX₂), BX₃ salts (BiX₃ and SbX₃), one BX₄ salt (SnX₄), and one BX₅ salt (SbX₅), where X represents any of three halide choices (I⁻, Br⁻ and Cl⁻). The A-site cations studied here were Na⁺, K⁺, Rb⁺ and Cs⁺.

The constituent atoms for adducts formed between the solvent and B-site cation salt complex were simulated in a dielectric medium of the corresponding solvent. In contrast, adducts formed between a solvent and an A-site cation were simulated in vacuum. DFT calculations were performed at 0 K with a PW6B95 functional that employed a dispersion correction for the solvent- BX_n enthalpies and a B97 functional with dispersion correction for the solvent- A^+ enthalpies; the functionals in which the models used to predict new DN/BF₃ and LCA values were based off, respectively. Coupled to both functionals, a triple-zeta basis set (def-TZVP), sufficient to avoid superposition errors [10], was used. The background and results for each group (BX₂, BX₃, BX₄, BX₅ and A⁺) are reported below.

Table S18: Solvent Properties: Solvent names and their acronyms in parentheses, the functional group of the solvent, Gutmann donor number, BF₃, and LCA. We have also reported the dielectric constants (ε) and acceptor number (AN) of these solvents and a few sources from perovskite literature in which these solvents were studied.

Solvent	Group	DN	BF ₃	LCA ^a	ε	AN	Lit. Sources
ACN	Nitrile	14.4	14.5	43.9	37.5	18.9	[11, 12]
PC	Carbonate	15.0	15.4	49.4	64.9	18.3	[13]
GBL	Ester	18.0	18.0	48.9	43.0	N/A	[14, 15]
ACE	Ketone	18.1	18.2	44.9	20.7	12.5	[16]
THF	Ether	20.6	21.7	43.3	7.6	8.0	[17]
DMF	Amide	26.6	26.5	52.9	36.7	16.0	[18, 19, 12, 20]
DMAC	Amide	27.8	26.9	54.0	37.8	13.6	[21]
NMP	Amide	27.3	27.0	55.9	32.0	13.3	[18, 12, 20]
DMI	Urea	27.6	23.7	57.1	37.6	N/A	[22]
DEF	Amide	30.9	27.2	55.9	29.0	N/A	[23]
DMSO	Sulfoxide	29.8	25.3	53.3	47.0	19.3	[19, 12, 20]
THIOUREA	Thiourea	31.8 ^{<i>a</i>}	15.5 ^{<i>a</i>}	45.0	30.0	N/A	[24, 25]
THTO	Sulfoxide	32.0 ^{<i>a</i>}	26.0 ^{<i>a</i>}	55.3	42.9	N/A	[12, 20, 15]
DMTF	Thioamide	33.0 ^a	15.8 ^{<i>a</i>}	45.2	42.8	18.8	[18]
DMPU	Urea	33.0	27.0	59.6	36.0	N/A	[13]
PYRIDINE	Azarane	33.5	30.7	45.5	12.4	14.2	[26]
MA	Amine	37.5 ^{<i>a</i>}	34.6 ^{<i>a</i>}	41.8	9.4	N/A	[27, 28, 29, 30]
HMPA	Phosphoramide	38.8	28.2	63.9	30.0	10.6	[31]

^a Values determined via linear model predictions

6. Background: BX₂ Salts in Perovskite Synthesis

Salts with the formula BX₂ (PbX₂, SnX₂, and GeX₂) are reagents that can be used to form 3D perovskites, and are the most popular sub-group of halide perovskite materials [32, 33, 34, 35]. These salts involve a +2 oxidation state and group 14 atoms with two halides (Cl⁻, Br⁻ or I⁻) bound to its atomic center. The coordination of solvents to these molecules have been studied both computationally and experimentally, with an overwhelming focus on PbX₂ salts [18, 20, 34, 35, 36, 37]. A particularly strong focus has been placed on PbI₂, the B-site cation salt of the highly efficient perovskite combination (PbMAI₃) which held the record for the most efficient perovskite solar cell, with an efficiency of 22% in 2017 [38]. Moreover, the Gutmann donor number was originally shown to correlate with the efficacy of solvents in a PbI₂ solution [13, 39].

Here, we present the binding enthalpies of solvents towards a more expansive pool of BX₂ salt complexes in Tables S19, S20 and S21, which includes lead(II), tin(II) [40, 41] and germanium(II) [42, 43] halide salts. From Table S31 our results indicate that the DN has a stronger correlation with BX₂ salt complexes than does the BF₃ scale. The R^2 value range for the DN is between 0.91 and 0.98, compared to a range of 0.31-0.44 for the BF₃ scale. Tables S19, S20, and S21 provides complementary binding enthalpy results. The superiority of the DN over the BF₃ scale is due, we believe, to the S-donor solvent's (Thiourea and DMTF) strong interaction with these salt complexes, resulting in a relatively strong interaction with $SbCl_5$ in the DN (32-33 kcal/mol), but a much weaker coordination to BF_3 (15-16 kcal/mol), as we have shown in an earlier section of the manuscript. In addition, the binding enthalpies of solvents to BX2 salt complexes is highest when the B-site cation and halide choices are Ge²⁺ and I⁻, respectively. Lastly, when we look at the coordination of halides to these salt complexes, chloride ions have a stronger binding preference to the various BX₂ salt complexes relative to the other two halides. The second strongest binding arises with bromide ions, followed by iodide ions; thus following a trend in electronegativity. Figures S14, S15, and S16 and Table S22 show the impact of the dielectric medium on halide coordination strengths. Table 3 in the main text presents the linear model derived from a correlation between the DN and BX₂ salt complexes.



Figure S13: Schematic of solvent- BX_2 adduct formation, which led to the determination of the PbX_2 , SnX_2 , and GeX_2 affinity scale. Color code as in the inset.



Figure S14: a-c) Binding enthalpies of PbX₂ salt complexes versus DN. The R^2 , slope (b₁) and intercept (b₀) determined from the linear fit (solid black lines) of the DN to the enthalpy data from DFT is written in the figure. Color code as in the inset. d-f) The effect of a medium's dielectric constant on the coordination strength of halides to PbX₂ salt complexes. An inverse relationship, with an apparent long range decay, between the coordination strength of each halide and the dielectric of the medium can be observed. Color code as in the inset.



Figure S15: a-c) Binding enthalpies of SnX_2 salt complexes versus DN. The R^2 , slope (b₁) and intercept (b₀) determined from the linear fit (solid black lines) of the DN to the enthalpy data from DFT is written in the figure. Color code as in the inset. d-f) The effect of a medium's dielectric constant on the coordination strength of halides to SnX_2 salt complexes. An inverse relationship, with an apparent long range decay, between the coordination strength of each halide and the dielectric of the medium can be observed. Color code as in the inset.

Table S19: Binding enthalpies (in kcal/mol) between various Lead Halides, PbX_2 , and 18 different solvents.

l_2
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Table S20: Binding enthalpies (in kcal/mol) between various Tin(II) Halides, SnX_2 , and 18 different solvents.

Solvent	SnI_2	SnBr ₂	SnCl ₂
ACN	11.0	10.9	10.4
PC	11.8	11.9	11.5
GBL	13.3	13.5	13.2
ACE	13.5	13.5	13.2
THF	17.0	17.0	16.8
DEF	18.8	20.9	16.7
NMP	19.2	19.2	18.7
DMF	19.7	19.4	18.8
DMAC	19.7	19.8	19.3
DMI	20.4	20.0	19.5
DMPU	21.2	21.2	20.9
DMTF	21.7	21.0	20.1
DMSO	22.3	21.0	21.2
THIOUREA	22.3	21.8	20.9
THTO	22.4	22.2	21.6
MA	23.0	22.9	21.5
PYRIDINE	23.5	20.9	20.3
HMPA	26.1	25.6	25.1

Table S21: Binding enthalpies (in kcal/mol) between various Germanium Halides, GeX₂, and 18 different solvents.

Solvent	GeI ₂	GeBr ₂	GeCl ₂
PC	12.8	13.2	13.0
ACN	13.2	12.8	12.0
GBL	14.7	14.9	14.4
ACE	15.7	15.9	15.3
THF	17.7	17.9	17.5
DMF	22.8	22.8	21.8
NMP	23.0	23.0	22.2
DMAC	23.1	23.3	22.4
DMI	23.3	23.1	22.1
DMSO	24.5	24.4	23.5
DEF	24.6	24.5	23.3
DMTF	25.2	24.2	22.8
THIOUREA	25.7	24.8	23.2
THTO	26.0	25.8	24.7
DMPU	26.6	25.4	24.7
PYRIDINE	27.0	24.7	23.8
MA	28.9	28.8	27.6
HMPA	30.0	29.5	28.3



Figure S16: a-c) Binding enthalpies of GeX_2 salt complexes versus DN. The R^2 , slope (b₁) and intercept (b₀) determined from the linear fit (solid black lines) of the DN to the enthalpy data from DFT is written in the figure. Color code as in the inset. d-f) The effect of a medium's dielectric constant on the coordination strength of halides to GeX_2 salt complexes. An inverse relationship, with an apparent long range decay, between the coordination strength of each halide and the dielectric of the medium can be observed. Color code as in the inset.

Perovskite Acid	Halide	$\varepsilon = 10$	$\varepsilon = 25$	$\varepsilon = 40$	$\varepsilon = 70$
	Ι-	22.0	20.2	19.8	19.4
PbI ₂	Br^-	24.0	21.8	21.3	20.9
	Cl^{-}	27.5	25.1	24.5	24.1
	I^-	21.5	19.8	19.3	19.0
PbBr ₂	Br^-	23.7	21.6	21.1	20.7
	Cl^{-}	27.3	25.0	24.4	24.0
	Ι-	20.5	18.8	18.3	18.0
PbCl ₂	Br^-	22.7	20.7	20.2	19.9
	Cl^{-}	26.4	24.1	23.6	23.2
	Ι-	21.9	20.0	19.5	19.2
SnI ₂	Br^-	24.4	22.1	21.5	21.2
	Cl^{-}	28.8	26.1	25.5	25.1
	Ι-	20.9	19.1	18.7	18.4
SnBr ₂	Br^-	23.6	21.5	21.0	20.6
	Cl^{-}	28.2	25.8	25.2	24.8
	Ι-	19.6	17.9	17.5	17.2
SnCl ₂	Br^-	22.5	20.5	20.0	19.6
	Cl^{-}	27.0	24.8	24.2	23.8
	Ι-	23.3	21.8	21.5	21.2
GeI ₂	Br^-	26.1	24.3	23.8	23.5
	Cl^{-}	31.1	28.9	28.4	28.0
	Ι-	22.1	20.7	20.4	20.1
GeBr ₂	Br^-	25.2	23.5	23.1	22.7
-	Cl^{-}	30.3	28.3	27.8	27.5
	Ι-	20.1	18.8	18.5	18.3
GeCl ₂	Br^-	23.3	21.7	21.3	21.0
	Cl^{-}	28.5	26.6	26.1	25.8

Table S22: Influence of the dielectric constant of the medium on the coordination strength of halides to BX_2 salt complexes. Results are presented for dielectric constants of 10, 25, 40, and 70.

7. Background: BX₃ Salts in Perovskite Synthesis

BX₃ salts (such as BiX₃ and SbX₃) are common reagents in the preparation of 2D perovskites [33, 44, 45] with a chemical formula of $A_3B_2X_9$, forming either a 2D layered or a 0D dimer structure. Solar cell efficiencies of this sub-group of perovskites are generally lower than their 3D counterparts. Salts with a BX₃ formula consists of ions in a +3 oxidation state from group 15 of the periodic table (*e.g.*, Bi(III) and Sb(III)). These salts comprise the B-site cation bound to three halide ions (Cl⁻, Br⁻, and I⁻) to achieve charge neutrality and stability of the salt complex. Preparation of perovskites from BX₃ salts often involves the inclusion of A-site cation salts, providing additional halides and a charge-balancing A-site cation to achieve photovoltaic capabilities [45, 46, 47, 48, 49]. However, it has also been reported that BX₃ salts, particularly bismuth salts, can also be processed as a stand-alone reagent to yield photovoltaically active thin films [50]. Nonetheless, the coordination of solvents to these salts also plays a role in the final morphology of the thin film.

In Table S31, we present the correlation we observed between binding enthalpies of solvents to BX₃ salt complexes and the explored affinity scales (the DN, BF₃, and LCA). In this case, the DN correlated well with the salt complexes ($R^2 = 0.91-0.93$), whereas the BF₃ metric correlated less strongly with the affinity of solvents for BX₃ salt complexes ($R^2 = 0.31-0.64$). Similar to the results we found for BX₂ salt complexes, the coordination of the salt complexes to chloride ions is favoured over Br⁻ and I⁻, in that order. In general, bismuth salt complexes exhibited stronger interactions with the solvents we studied than their antimony tri-halide counterparts. But the interaction strength between solvents and BX₃ salt complexes is generally weaker than those with BX₂ complexes. Tables S23 and S24 provide the corresponding binding enthalpy results. Figures S18 and S19, as well as Table S25 show the impact of the dielectric medium on halide coordination strengths. Table 3 in the main text presents the linear model derived from a correlation between the DN and BX₃ salt complexes.



Figure S17: Schematic of solvent-BX₃ adduct formation, which led to the determination of the BiX_3 and SbX_3 affinity scale. Color code as in the inset.



Figure S18: a-c) Binding enthalpies of BiX₃ salt complexes versus DN. The R^2 , slope (b₁) and intercept (b₀) determined from the linear fit (solid black lines) of the DN to the enthalpy data from DFT is written in the figure. Color code as in the inset. d-f) The effect of a medium's dielectric constant on the coordination strength of halides to BiX₃ salt complexes. An inverse relationship, with an apparent long range decay, between the coordination strength of each halide and the dielectric of the medium can be observed. Color code as in the inset.



Figure S19: a-c) Binding enthalpies of SbX₃ salt complexes versus DN. The R^2 , slope (b₁) and intercept (b₀) determined from the linear fit (solid black lines) of the DN to the enthalpy data from DFT is written in the figure. Color code as in the inset. d-f) The effect of a medium's dielectric constant on the coordination strength of halides to SbX₃ salt complexes. An inverse relationship, with an apparent long range decay, between the coordination strength of each halide and the dielectric of the medium can be observed. Color code as in the inset.

Table S23: Binding enthalpies (in kcal/mol) between various Bismuth Halides, BiX_3 , and 18 different solvents.

Solvent	BiI ₃	BiBr ₃	BiCl ₃
ACN	5.3	6.2	6.4
PC	6.9	7.5	7.7
GBL	7.6	8.7	9.0
ACE	8.0	9.0	8.4
NMP	10.6	11.9	12.1
THF	10.8	11.8	11.5
DMAC	11.1	12.6	12.8
DMF	11.7	12.9	13.0
DEF	12.2	13.6	13.8
DMI	12.3	13.5	13.6
DMSO	12.5	13.8	14.1
DMPU	12.8	14.0	14.0
DMTF	13.0	13.5	12.4
THTO	13.7	14.9	15.1
THIOUREA	13.7	13.9	13.2
PYRIDINE	15.2	15.6	15.4
MA	15.8	17.1	17.2
HMPA	15.9	17.2	17.2

Table S24: Binding enthalpies (in kcal/mol) between various Antimony(III) Halides, SbX₃, and 18 different solvents.

Solvent	SbI ₃	SbBr ₃	SbCl ₃
ACN	3.5	4.1	4.3
PC	5.0	5.3	5.4
GBL	5.5	6.6	6.8
ACE	5.6	6.4	6.6
NMP	8.7	10.1	10.2
THF	8.8	9.6	9.5
DMAC	9.1	10.6	10.9
DMF	9.2	10.4	10.4
DMI	9.5	10.1	10.3
DEF	10.2	11.4	11.8
DMSO	10.2	11.6	11.1
THTO	10.2	11.4	11.6
PYRIDINE	10.2	13.4	11.3
DMTF	11.4	11.6	11.0
DMPU	11.5	12.7	12.9
THIOUREA	11.8	11.8	11.0
HMPA	13.8	14.3	13.8
MA	15.1	16.4	15.6

Perovskite Acid	Halide	$\varepsilon = 10$	$\varepsilon = 25$	$\varepsilon = 40$	$\varepsilon = 70$
	I–	15.8	14.0	13.5	13.2
BiI ₃	Br^-	17.3	15.1	14.6	14.2
	Cl^{-}	20.5	18.1	17.5	17.1
	Ι-	16.0	14.2	13.8	13.5
BiBr ₃	Br^-	18.0	15.9	15.3	15.0
	Cl^{-}	21.6	19.2	18.6	18.2
	Ι-	15.0	13.2	12.8	12.5
BiCl ₃	Br^-	17.2	15.1	14.6	14.3
	Cl^{-}	20.9	18.6	18.0	17.6
	Ι-	12.2	10.6	10.2	9.9
SbI ₃	Br^-	13.8	11.8	11.4	11.0
	Cl^{-}	17.5	15.3	14.7	14.3
	Ι-	12.1	10.6	10.2	9.9
SbBr ₃	Br^-	14.2	12.3	11.8	11.5
	Cl^{-}	18.3	16.1	15.6	15.2
	Ι-	11.0	9.4	9.1	8.8
SbCl ₃	Br^-	13.2	11.4	10.9	10.6
	Cl^{-}	17.3	15.2	14.7	14.3

Table S25: Influence of the dielectric constant of the medium on the coordination strength of halides to BX_3 salt complexes. Results were explored for dielectric constants of 10, 25, 40, and 70.

8. Background: BX₄ Salts in Perovskite Synthesis

 BX_4 salts arise from group 14 atoms with oxidation states of +4. Some group 14 atoms are more stable in their +2 oxidation state, but elements like Sn exhibit a +4 oxidation state that is more stable than its Sn(II) oxidation counterpart, leading to the formation of salts with four halides bound to the central ion. In fact, Sn(II) complexes have been shown to oxidize to more stable Sn(IV) complexes when exposed to air [51, 52].

In this study, the only class of BX_4 salts we explored are the salts formed with the Sn(IV) cation (SnX_4 salts) and, like the BX_3 salts, the +4 oxidation state of cations in BX_4 salts creates a sub-class of perovskite structures. 3D vacancy-ordered double perovskites with a chemical formula of A_2BX_6 [53] form as a result of this change in oxidation state to maintain stoichiometric and charge balance [33, 44, 54]. The use of SnX_4 salts has been reported to lead to the production of films that are stable in air and moisture relative to their ABX_3 perovskite counterparts from SnX_2 salts [55, 56].

We determined the efficacy of the DN and BF_3 metrics to describe the strength of interaction between solvents and SnX_4 salt complexes. The results from Table S31 indicated that there is a stronger correlation with the DN than with BF_3 , consistent with the trends we observed for the BX_2 and BX_3 salt complexes. For the DN, the correlation ranged between R^2 values of 0.94-0.95, while those for the BF_3 metric ranged between 0.51-0.60. Again, we observed a higher coordination strength of chloride ions to these complexes, with I⁻ being the weakest of the three halides. Figures S21 and Table S27 show the impact of the dielectric medium on the halide coordination strengths. Unlike the BX_2 and BX_3 salt groups, however, the coordination of solvents to the $SnCl_4$ salt complex was stronger than the coordination of solvents to $SnBr_4$ and SnI_4 salt complexes. See Table S26 for binding enthalpy results. Table 3 in the main text presents the linear model derived from a correlation between the DN and BX_4 salt complexes.



Figure S20: Schematic of solvent- BX_4 adduct formation, which led to the determination of the SnX_4 affinity scale. Color code as in the inset.

Table S26: Binding enthalpies (in kcal/mol) between various Tin(IV) Halides, SnX_4 , and 18 different solvents.

Solvent	SnI_4	SnBr ₄	SnCl ₄
ACN	1.6	4.3	6.7
PC	3.1	6.1	8.2
GBL	3.6	7.0	9.3
ACE	4.2	7.7	9.9
THF	7.6	10.6	12.7
DMAC	9.3	13.8	16.3
DMI	9.4	14.1	16.7
DMF	9.7	14.2	17.0
NMP	9.9	14.5	17.2
DMPU	10.3	15.3	18.3
DEF	10.9	15.2	17.7
DMTF	11.1	15.5	18.0
THTO	11.4	17.3	19.5
THIOUREA	11.8	14.3	17.1
DMSO	12.3	16.5	18.7
PYRIDINE	12.5	17.2	20.1
MA	16.4	21.8	24.9
HMPA	16.6	21.2	23.8

Table S27: Influence of the dielectric constant of the medium on the coordination strength of halides t	0
BX ₄ salt complexes. Results were explored for dielectric constants of 10, 25, 40, and 70.	

Perovskite Acid	Halide	$\varepsilon = 10$	$\varepsilon = 25$	$\varepsilon = 40$	$\varepsilon = 70$
	Ι-	8.7	7.1	6.7	6.5
SnI_4	Br^-	10.6	8.6	8.1	7.7
	Cl^{-}	15.5	13.1	12.6	12.2
	Ι-	13.6	12.1	11.7	11.4
SnBr ₄	Br^-	16.6	14.7	14.3	13.9
	Cl^{-}	21.6	19.5	18.9	18.5
	I^-	16.0	14.6	14.2	14.0
SnCl ₄	Br^-	19.3	17.5	17.1	16.7
	Cl^{-}	24.9	22.7	22.2	21.8



Figure S21: a-c) Binding enthalpies of SnX_4 salt complexes versus DN. The R^2 , slope (b₁) and intercept (b₀) determined from the linear fit (solid black lines) of the DN to the enthalpy data from DFT is written in the figure. Color code as in the inset. d-f) The effect of a medium's dielectric constant on the coordination strength of halides to SnX_4 salt complexes. An inverse relationship, with an apparent long range decay, between the coordination strength of each halide and the dielectric of the medium can be observed. Color code as in the inset.

9. Background: BX₅ Salts in Perovskite Synthesis

The last of the B-site cation salt groups we studied involved BX_5 salts. These salts comprise cations having a +5 oxidation state for group 15 elements bound to five halides. The only salts studied in this group are SbX₅ salts, which produce newly explored perovskites with a chemical formula of ABX₆ [57]. Despite their observed photovoltaic activity, these perovskites exhibit stability and performance issues that warrant exploration of new complexes to understand these issues [57, 58]. Correspondingly, solvent impacts on the processing of these perovskites have yet to be explored. Given that SbCl₅ (the reference Lewis acid for the DN) is part of this sub-group, it is reasonable to expect that the DN will correlate well with the binding enthalpy of solvents to these salt complexes, and better than the correlation for BF₃.

This supposition was confirmed, as shown in Table S31. For the DN, the correlation ranged from R^2 values of 0.98-0.99, whereas the correlation for the BF_3 metric ranged from 0.43-0.50. There was a consistent trend in ranking the strength of the halide ion coordination to these salt complexes that mirrored the halide electronegativity. Figure S23 and Table S29 show the impact of the dielectric medium on the halide coordination strengths. Finally, the strongest solvent-salt complex coordination observed within this sub-group occurred between solvents and the SbCl₅ salt complex. Solvent-SbI₅ interactions ranked lowest of the three salt complexes, as observed in the case of SnX₄ salt complexes. The binding enthalpy results for these salt complexes are also listed in Table S28. Table 3 in the main text presents the linear model derived from a correlation between the DN and BX₅ salt complexes.



Figure S22: Schematic of solvent-BX₅ adduct formation, which led to the determination of the SbX₅ affinity scale. Color code as in the inset.

Solvent	SbI ₅	SbBr ₅	SbCl ₅
ACN	6.9	11.1	14.7
PC	8.1	12.3	15.9
GBL	9.5	14.1	18.0
ACE	10.2	14.6	18.6
DMF	18.1	23.9	28.2
NMP	18.5	24.2	28.2
DMI	19.1	25.0	29.1
DMAC	19.2	24.9	28.7
DEF	21.6	26.9	30.5
PYRIDINE	22.5	28.9	33.5
DMPU	22.8	28.7	32.7
THIOUREA	23.0	28.3	31.7
DMSO	23.1	28.0	31.4
DMTF	23.6	29.2	31.9
THTO	24.2	29.0	32.5
HMPA	26.7	32.7	37.2
MA	27.0	33.5	37.5

Table S28: Binding enthalpies (in kcal/mol) between various Antimony(V) Halides, Sb X_5 , and 18 different solvents.

Table S29: Influence of the dielectric constant of the medium on the coordination strength of halic	les to
BX_5 salt complexes. Results were explored for dielectric constants of 10, 25, 40, and 70.	

Perovskite Acid	Halide	$\varepsilon = 10$	$\varepsilon = 25$	$\varepsilon = 40$	$\varepsilon = 70$
	I^-	22.1	20.5	20.0	19.7
SbI ₅	Br^-	23.7	21.6	21.1	20.7
	Cl^{-}	28.6	26.3	25.7	25.3
	Ι-	27.5	26.0	25.7	25.4
SbBr ₅	Br^-	29.4	27.5	27.1	26.7
	Cl^{-}	34.7	32.5	31.9	31.5
	I-	30.7	29.3	29.0	28.8
SbCl ₅	Br^-	32.9	31.1	30.7	30.4
	Cl^{-}	38.4	36.4	35.8	35.4



Figure S23: a-c) Binding enthalpies of SbX_5 salt complexes versus DN. The R², slope (b₁) and intercept (b₀) determined from the linear fit (solid black lines) of the DN to the enthalpy data from DFT is written in the figure. Color code as in the inset. The effect of a medium's dielectric constant on the coordination strength of halides to SbX_5 salt complexes. d-f) An inverse relationship, with an apparent long range decay, between the coordination strength of each halide and the dielectric of the medium can be observed. Color code as in the inset.



Figure S24: Theshold DN values for halides bound to BX_n salt complexes in a dielectric medium of 25 and 70. The DN values for each halide are indicative of the minimum DN of a solvent required to yield a binding enthalpy higher than the pertinent halides (Cl⁻, Br⁻ and I⁻) at 0 K and in different dielectric media. These values were determined by inputting the halide enthalpies for each BX_n salt complex reported in Table 3 in the main text to the inverse of the linear model for that system i.e. $DN = (BE_{Halide} - b_0)/b_1$; the error bars are associated with the MAE of each model i.e. MAE/b₁. We also included horizontal lines to represent the DN's of five solvents HMPA (DN = 38.8), DMPU (DN = 33.0), DMSO (DN = 29.8), DMF (DN = 26.7) and GBL (DN = 18.0) to compare with the halide values for each BX_n salt complex. Results show that the dielectric of the medium impacts the DN threshold values for each Ax_n salt complex. Which increases in lower dielectric mediums.

10. Background: Solvent to A-site Cation Interactions

The importance of the interaction between solvents and A-site cations has often been overlooked in the literature, with a lot more attention being focused on the role of B-site cation salts. A recent study by Moot *et al.* of the interaction between DMSO and DMF solvents and Cs^+ has suggested that A-site cation interactions might play a more important role in the nucleation and growth of perovskite crystals than previously understood [59]. This suggests that other ions from the alkaline earth metals, (*e.g.*, Na⁺, K⁺, Rb⁺ and Cs⁺) could, in principle, influence the solution processing of all-inorganic perovskite solutions [57, 60, 61, 62, 63]. Thus, consideration of the interactions between solvents and A-site cations should not be overlooked.

Due to the similarity between these four group 1 cations and Li^+ , we focused on using the LCA scale for this study. The results in Table S31 suggest that the LCA metric correlates well with these ions, showing an R^2 range of 0.94-0.98. Table S30 lists the complementary results for the binding enthalpies and Figure S26 shows their correlation with the LCA. Interestingly, the interaction strength between solvents and A-site cations are progressively weaker for the other group 1 cations compared to that for Li^+ , suggesting that a group trend (*e.g.*, size or ionization) influences the strength of the interaction between the LCA metric and these four A-site cations is shown in Table 3 in the main text.



Figure S25: Schematic of solvent-A⁺ adduct formation, which led to the determination of the NCA, KCA, RCA and CCA affinity scale. Color code as in the inset.



Figure S26: Binding enthalpies of A^+ ions versus LCA. The R^2 , slope (b₁) and intercept (b₀) determined from the linear fit (solid black lines) of the LCA to the enthalpy data from DFT is written in the figure. Color code as in the inset.

Table S30: Binding enthalpies (in kcal/mol) between four group 1 cations, Na⁺, K⁺, Rb⁺ and Cs⁺, and 18 different solvents resulting in the Sodium Cation Affinity (NCA), Potassium Cation Affinity (KCA), Rubidium Cation Affinity (RCA), and Cesium Cation Affinity (CCA).

Solvent	NCA	KCA	RCA	CCA
MA	30.1	21.2	18.4	16.6
THF	30.7	22.4	19.5	17.7
ACE	32.6	24.3	21.5	19.4
ACN	32.6	24.4	21.5	19.4
PYR	32.7	23.0	20.0	17.8
THIOUREA	34.4	24.7	22.1	21.0
DMTF	34.6	25.2	22.4	20.5
GBL	36.4	27.7	24.6	22.3
PC	36.9	28.2	25.2	22.9
DMF	38.9	28.9	25.5	23.8
DMSO	39.5	30.3	26.9	24.7
DMAC	40.7	30.8	27.3	23.6
THTO	40.9	31.4	28.0	25.7
NMP	41.2	31.3	27.8	25.3
DEF	41.3	31.4	27.9	25.5
DMI	42.0	31.8	28.2	25.7
DMPU	43.6	33.1	29.3	26.9
HMPA	46.9	36.2	32.3	30.0



Figure S27: ¹³³Cs NMR spectra of 20mM CsI in mixtures of NMP & NMPT. From top to bottom, the spectra represent 15%, 25%, 37.5%, 50%, 75% and 100% NMP. Peak broadening is observed when NMPT is introduced due to the presence of an asymmetric chemical environment around Cs^+ as well as possible chemical exchange.



Figure S28: ¹³³Cs NNMR spectra of 20mM CsI in mixtures of DMF & DMTF. From top to bottom, the spectra represent 5%, 10%, 20%, 40%, 60%, 80% and 100% DMF. Peak broadening is observed when DMTF is introduced due to the presence of an asymmetric chemical environment around Cs^+ as well as possible chemical exchange.



Figure S29: ⁸⁷Rb NMR spectra of 200mM RbI in mixtures of NMP & NMPT. From top to bottom, the spectra represent 40%, 50%, 60%, 80% and 100% NMP. Peak broadening is observed when NMPT is introduced due to the presence of an asymmetric chemical environment around Rb⁺ as well as possible chemical exchange.



Figure S30: ⁸⁷Rb NMR spectra of 200mM RbI in mixtures of DMF & DMTF. From top to bottom, the spectra represent 30%, 40%, 50%, 60%, 80% and 100% DMF. Peak broadening is observed when DMTF is introduced due to the presence of an asymmetric chemical environment around Rb⁺ as well as possible chemical exchange.

11. Correlation and Accuracy of Linear Models

In this section, we present the R^2 results which highlights the Gutmann donor number's correlation with solvent- BX_n interactions and the LCA's correlation to solvent- A^+ interactions. Table S31 shows correlation results that include S-donor solvents (DMTF and Thiourea) in the fitting process; whereas Table S32 excludes S-donor solvents in the fitting, which resulted in a substantial increase in R^2 between the solvent- BX_n interactions and the BF₃ scale. We explored the ability of our previously reported linear models to predict the binding affinity of nine solvents, distinct by functional group, to the aforementioned perovskite species. Tables S34 to S41 provide the accuracy of our linear models.

Table S31: Consolidation of the R² correlation results for solvent-BX_n interactions and solvent-A⁺ interactions as expressed using the Gutmann donor number, BF₃, and LCA affinity scales. Data in bold highlight the best correlation for a given species, showing the superiority of the DN for BX_n salt complex interactions and of the LCA for A-site cation interactions. Results in this table **include** fitting towards S-donor solvents (DMTF and Thiourea).

Perovskite Acids	DN(R ²)	$BF_3(R^2)$	$LCA(R^2)$
PbI ₂	0.95	0.31	0.12
PbBr ₂	0.91	0.33	0.12
PbCl ₂	0.93	0.35	0.05
SnI ₂	0.93	0.41	0.14
SnBr ₂	0.96	0.44	0.13
SnCl ₂	0.91	0.42	0.12
GeI ₂	0.98	0.49	0.11
GeBr ₂	0.96	0.51	0.13
GeCl ₂	0.95	0.55	0.13
BiI ₃	0.92	0.37	0.07
BiBr ₃	0.93	0.55	0.11
BiCl ₃	0.91	0.64	0.15
SbI ₃	0.91	0.40	0.06
SbBr ₃	0.92	0.57	0.06
SbCl ₃	0.91	0.60	0.10
SnI ₄	0.94	0.51	0.10
SnBr ₄	0.94	0.59	0.13
SnCl ₄	0.95	0.60	0.12
SbI ₅	0.98	0.43	0.12
SbBr ₅	0.98	0.45	0.14
SbCl ₅	0.99	0.50	0.14
Na ⁺	0.13	0.09	0.98
K^+	0.08	0.06	0.97
Rb^+	0.08	0.05	0.96
Cs^+	0.09	0.04	0.94

Table S32: Consolidation of the R^2 correlation results for solvent- BX_n interactions and solvent- A^+ interactions as expressed using the Gutmann donor number, BF_3 , and LCA affinity scales. Data in bold highlight the best correlation for a given species, showing the superiority of the DN for BX_n salt complex interactions and of the LCA for A-site cation interactions. Results in this table **exclude** fitting towards S-donor solvents (DMTF and Thiourea).

Perovskite Acids	$DN(R^2)$	$BF_3(R^2)$	$LCA(R^2)$
PbI ₂	0.95	0.83	0.24
PbBr ₂	0.91	0.80	0.25
PbCl ₂	0.93	0.90	0.12
SnI ₂	0.93	0.80	0.24
SnBr ₂	0.97	0.87	0.21
SnCl ₂	0.91	0.81	0.19
GeI ₂	0.98	0.91	0.18
GeBr ₂	0.97	0.90	0.19
GeCl ₂	0.97	0.90	0.18
BiI ₃	0.93	0.86	0.13
BiBr ₃	0.94	0.87	0.15
BiCl ₃	0.95	0.87	0.18
SbI ₃	0.91	0.84	0.14
SbBr ₃	0.92	0.92	0.10
SbCl ₃	0.93	0.90	0.14
SnI ₄	0.95	0.87	0.16
SnBr ₄	0.96	0.89	0.17
SnCl ₄	0.97	0.91	0.17
SbI ₅	0.98	0.86	0.22
SbBr ₅	0.98	0.89	0.22
SbCl ₅	0.99	0.90	0.22
Na ⁺	0.14	0.09	0.99
K^+	0.08	0.06	0.97
Rb^+	0.08	0.04	0.96
Cs^+	0.09	0.04	0.96

Table S33: Solvent properties for test cases: Solvent names and their acronyms in parentheses, the functional group of the solvent, Gutmann donor number, BF₃, and LCA. We also report the dielectric constants (ε) and acceptor number (AN) of these solvents and some appropriate literature sources.

Solvent	Group	DN	BF ₃	LCA	ε	AN	Lit. Sources
NMPT	Thioamide	32.4 ^{<i>a</i>}	16.3 ^{<i>a</i>}	47.8 ^{<i>a</i>}	32.0^{b}	N/A	[18]
DESO	Sulfoxide	33.5 ^{<i>a</i>}	27.1^{a}	55.3 ^{<i>a</i>}	42.0	N/A	N/A
FORMAMIDE	Amide	24.0	23.6 ^{<i>a</i>}	48.5 ^{<i>a</i>}	111.0	39.8	N/A
PROPIONITRILE	Nitrile	16.1	14.6	45.4	28.0	N/A	[64]
EC	Carbonate	15.0	15.9	47.9 ^{<i>a</i>}	95.0	N/A	[65]
DE	Ether	19.0	19.0	43.2 ^{<i>a</i>}	4.3	3.9	[66]

^a Values determined via linear model predictions

^b NMPT's dielectic constant value was set to 32, the value of NMP, due to the unavailability of this value in literature (after an exhaustive search)

Table S34: Comparison of test cases of binding enthalpies predicted by our linear models compared to DFT-calculated values for PbX_2 salt complexes.

Solvent	DFT (kcal/mol)	Model (kcal/mol)	DFT-Model (kcal/mol)
PbI ₂ : 0.53DN + 3.6			
NMPT	21.3	20.8	0.5
DESO	20.1	21.4	1.3
FORMAMIDE	16.0	16.3	0.3
PROPIONITRILE	11.0	12.1	1.1
EC	11.3	11.6	0.3
DE	14.4	13.7	0.7
			MAE error = 0.7 kcal/mol
PbBr ₂ : 0.47 DN + 4.8			
NMPT	20.7	20.0	0.7
DESO	19.7	20.5	0.8
FORMAMIDE	16.1	16.1	0.0
PROPIONITRILE	11	12.3	1.3
EC	11.3	11.9	0.6
DE	14.5	13.7	0.8
			MAE error = 0.7 kcal/mol
PbCl ₂ : 0.48DN + 4.3			
NMPT	19.7	19.9	0.2
DESO	19.0	20.4	1.4
FORMAMIDE	15.9	15.8	0.1
PROPIONITRILE	12.0	12.0	0.0
EC	11.1	11.5	0.4
DE	14.4	13.4	1.0
			MAE error = 0.5 kcal/mol

Solvent	DFT (kcal/mol)	Model (kcal/mol)	DFT-Model (kcal/mol)
SnI ₂ : 0.56DN + 3.8			
NMPT	22.2	21.9	0.3
DESO	21.9	22.6	0.7
FORMAMIDE	15.4	17.2	1.8
PROPIONITRILE	11.3	12.8	1.5
EC	11.4	12.2	0.8
DE	14.9	14.4	0.5
			MAE error = 0.9 kcal/mol
SnBr ₂ : 0.56DN + 3.7			
NMPT	21.2	21.8	0.5
DESO	21.3	22.5	1.2
FORMAMIDE	15.7	17.1	1.4
PROPIONITRILE	11.1	12.7	1.6
EC	11.5	12.1	0.6
DE	14.6	14.3	0.3
			MAE error = 0.9 kcal/mol
SnCl ₂ : 0.54DN + 3.6			
NMPT	20.1	21.1	1.0
DESO	20.7	21.7	1.0
FORMAMIDE	16.8	16.6	0.2
PROPIONITRILE	11.2	12.2	1.0
EC	10.8	11.7	0.9
DE	13.8	13.9	0.1
			MAE error = 0.7 kcal/mol

Table S35: Comparison of test cases of binding enthalpies predicted by our linear models compared to DFT-calculated values for SnX_2 salt complexes.

Solvent	DFT (kcal/mol)	Model (kcal/mol)	DFT-Model (kcal/mol)
GeI ₂ : 0.73DN + 2.7			
NMPT	26.6	26.4	0.2
DESO	26.1	27.2	1.1
FORMAMIDE	18.2	20.2	2.0
PROPIONITRILE	13.5	14.4	0.9
EC	13.0	13.7	0.7
DE	16.6	16.6	0.0
			MAE error = 0.8 kcal/mol
GeBr ₂ : 0.68DN + 3.6			
NMPT	25.5	25.6	0.1
DESO	26.6	26.4	0.2
FORMAMIDE	19.0	19.9	0.9
PROPIONITRILE	13.2	14.5	1.3
EC	12.9	13.8	0.9
DE	16.8	16.5	0.3
			MAE error = 0.6 kcal/mol
GeCl ₂ : 0.65DN + 3.5			
NMPT	23.5	24.6	1.1
DESO	25.9	25.3	0.6
FORMAMIDE	17.9	19.1	1.2
PROPIONITRILE	12.2	14.0	1.8
EC	12.7	13.3	0.6
DE	16.4	15.9	0.6
			MAE error = 1.0 kcal/mol

Table S36: Comparison of test cases of binding enthalpies predicted by our linear models compared to DFT-calculated values for GeX_2 salt complexes.

Solvent	DFT (kcal/mol)	Model (kcal/mol)	DFT-Model (kcal/mol)
BiI ₃ : 0.39DN + 0.8			
NMPT	13.9	13.3	0.5
DESO	14.4	13.9	0.5
FORMAMIDE	9.2	10.2	1.0
PROPIONITRILE	5.5	7.0	1.5
EC	6.6	6.7	0.1
DE	9.7	8.2	1.5
			MAE error = 0.8 kcal/mol
BiBr ₃ : $0.40DN + 1.6$			
NMPT	14.2	14.6	0.4
DESO	15.7	15.0	0.7
FORMAMIDE	10.6	11.2	0.6
PROPIONITRILE	6.4	8.0	1.6
EC	7.3	7.6	0.3
DE	10.5	9.2	1.3
			MAE error = 0.8 kcal/mol
BiCl₃: 0.39DN + 1.8			
NMPT	13.6	14.4	0.8
DESO	16.0	14.9	1.1
FORMAMIDE	10.9	11.2	0.3
PROPIONITRILE	6.6	8.0	1.4
EC	7.5	7.7	0.2
DE	10.8	9.2	1.6
			MAE error = 0.9 kcal/mol

Table S37: Comparison of test cases of binding enthalpies predicted by our linear models compared to DFT-calculated values for BiX_3 salt complexes.

Solvent	DFT (kcal/mol)	Model (kcal/mol)	DFT-Model (kcal/mol)
SbI ₃ : 0.39DN - 1.2			
NMPT	11.4	11.4	0.0
DESO	12.2	11.9	0.3
FORMAMIDE	7.0	8.2	1.2
PROPIONITRILE	4.0	5.0	1.0
EC	4.8	4.7	0.2
DE	7.7	6.2	1.5
			MAE error = 0.7 kcal/mol
SbBr ₃ : 0.41DN - 0.8			
NMPT	11.6	12.5	0.9
DESO	13.9	12.9	1.0
FORMAMIDE	8.3	9.0	0.7
PROPIONITRILE	4.3	5.8	1.5
EC	5.4	5.4	0.0
DE	8.2	7.0	1.2
			MAE error = 0.9 kcal/mol
SbCl ₃ : 0.38DN - 0.1			
NMPT	10.8	12.2	1.4
DESO	14.0	12.6	1.4
FORMAMIDE	9.7	9.0	0.7
PROPIONITRILE	4.4	6.0	1.6
EC	5.5	5.6	0.1
DE	8.5	7.1	1.4
			MAE error = 1.1 kcal/mol

Table S38: Comparison of test cases of binding enthalpies predicted by our linear models compared to DFT-calculated values for SbX_3 salt complexes.

Solvent	DFT (kcal/mol)	Model (kcal/mol)	DFT-Model (kcal/mol)
SnI ₄ : 0.55DN - 5.6			
NMPT	11.2	12.2	1.0
DESO	12.2	12.8	0.6
FORMAMIDE	6.1	7.6	1.5
PROPIONITRILE	1.8	3.3	1.5
EC	2.9	2.7	0.2
DE	5.0	4.9	0.1
			MAE error = 0.8 kcal/mol
SnBr ₄ : 0.64DN - 3.8			
NMPT	15.7	16.9	1.2
DESO	16.7	17.6	0.9
FORMAMIDE	10.4	11.6	1.2
PROPIONITRILE	4.7	6.5	1.8
EC	5.7	5.8	0.0
DE	7.6	8.36	1.4
			MAE error = 1.1 kcal/mol
SnCl ₄ : 0.66DN - 2.0			
NMPT	18.2	19.4	1.2
DESO	19.2	20.1	0.9
FORMAMIDE	13	13.7	0.8
PROPIONITRILE	6.9	8.5	1.7
EC	7.9	7.9	0.0
DE	9.2	10.5	1.3
			MAE error = 1.0 kcal/mol

Table S39: Comparison of test cases of binding enthalpies predicted by our linear models compared to DFT-calculated values for SnX_4 salt complexes.

Solvent	DFT (kcal/mol)	Model (kcal/mol)	DFT-Model (kcal/mol)
SbI ₅ : 0.86DN - 4.9			
NMPT	22.2	23.0	0.8
DESO	24.8	23.9	0.9
FORMAMIDE	13.6	15.7	2.1
PROPIONITRILE	7.2	8.9	1.7
EC	7.8	8.0	0.2
DE	9.2	11.4	2.2
			MAE error = 1.3 kcal/mol
SbBr ₅ : 0.94DN - 1.7			
NMPT	27.4	28.8	1.4
DESO	29.9	29.8	0.1
FORMAMIDE	19.5	20.9	1.4
PROPIONITRILE	11.5	13.4	1.9
EC	12.0	12.4	0.4
DE	13.3	16.2	2.9
			MAE error = 1.3 kcal/mol
SbCl ₅ : 0.95DN + 1.9			
NMPT	32.0	32.7	0.7
DESO	34.0	33.7	0.3
FORMAMIDE	23.5	24.7	1.2
PROPIONITRILE	17.1	17.2	0.1
EC	15.6	16.2	0.6
DE	19.6	20.0	0.4
			MAE error = 0.5 kcal/mol

Table S40: Comparison of test cases of binding enthalpies predicted by our linear models compared to DFT-calculated values for SbX_5 salt complexes.

Solvent	DFT (kcal/mol)	Model (kcal/mol)	DFT-Model (kcal/mol)
Na ⁺ : 0.74LCA - 0.2			
NMPT	36.8	35.1	1.6
DESO	40.8	40.7	0.1
FORMAMIDE	35.5	35.7	0.2
PROPIONITRILE	33.8	33.4	0.4
EC	35.7	35.2	0.5
DE	31.4	31.8	0.4
			MAE error = 0.6 kcal/mol
K ⁺ : 0.65LCA - 4.8			
NMPT	26.8	26.3	0.5
DESO	31.3	31.1	0.2
FORMAMIDE	26.8	26.7	0.1
PROPIONITRILE	25.2	24.7	0.5
EC	27.2	26.3	0.9
DE	21.9	23.3	1.4
			MAE error = 0.6 kcal/mol
Rb ⁺ : 0.59LCA - 5.1			
NMPT	23.8	23.1	0.7
DESO	27.8	27.5	0.3
FORMAMIDE	23.8	23.5	0.3
PROPIONITRILE	22.4	21.7	0.7
EC	24.3	23.2	1.1
DE	18.8	20.4	1.6
			MAE error = 0.8 kcal/mol
Cs ⁺ : 0.55LCA - 5.3			
NMPT	21.7	21.0	0.7
DESO	25.7	25.1	0.6
FORMAMIDE	21.6	21.4	0.2
PROPIONITRILE	20.2	19.7	0.5
EC	22.1	21.0	1.1
DE	16.8	18.5	1.7
			MAE error = 0.8 kcal/mol

Table S41: Comparison of test cases of binding enthalpies predicted by our linear models compared to DFT-calculated values for A-site cations.

12. Chemical Properties of Solvents and Lewis acids

In this section, we present useful chemical properties of the solvents and the Lewis acids explored in this study. The hardness and softness of each specie was determined from their Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) energy levels in DFT via a PW6B95 functional with dispersion and a tripe zeta basis set, which was used to determine the binding enthalpies for BX_n salt complexes in the previous sections and a top performer for the LCA estimation (see Table S5). The dipole moments and Unsaturated Mayer Bond Order (UMBO) of the solvents were also determined (see Table S42).

Solvent	HOMO	LUMO	η	$1/\eta$	χ	μ	UMBO
Oxygen donor solvents							
PC	-8.7	0.7	4.7	0.2	4.0	5.37	-0.13
EC	-8.8	0.6	4.7	0.2	4.1	5.25	-0.12
ACE	-7.4	-0.2	3.6	0.3	3.8	2.99	-0.10
BUTANONE	-7.3	-0.2	3.6	0.3	3.8	2.82	-0.09
GBL	-8.0	0.4	4.2	0.2	3.8	4.55	-0.10
THF	-7.2	1.1	4.2	0.2	3.0	1.78	0.02
FORMAMIDE	-7.8	0.7	4.2	0.2	3.5	3.86	0.02
DMF	-7.2	0.6	3.9	0.3	3.3	3.98	0.03
NMP	-7.0	0.9	4.0	0.3	3.1	3.92	0.00
DMAC	-7.0	0.9	4.0	0.3	3.1	3.78	0.02
DMSO	-6.8	1.0	3.9	0.3	2.9	3.76	0.20
DEF	-7.1	0.8	4.0	0.3	3.1	4.20	-0.01
DMPU	-6.6	0.7	3.6	0.3	2.9	3.98	0.17
HMPA	-6.4	0.7	3.5	0.3	2.9	3.62	-0.12
DBSO	-9.4	0.5	5.0	0.2	4.5	3.55	0.29
DMI	-6.7	1.0	3.9	0.3	2.9	3.84	0.07
DESO	-6.6	0.8	3.7	0.3	2.9	3.58	0.26
ТНТО	-6.6	0.8	3.7	0.3	2.9	4.00	0.23
UREA	-7.6	0.5	4.1	0.2	3.6	4.28	-0.01
DE	-7.4	1.3	4.4	0.2	3.1	1.14	0.04
Nitrogen donor solvents							
ACN	-9.6	0.8	5.2	0.2	4.4	3.99	-0.02
PYRIDINE	-7.5	-0.7	3.4	0.3	4.1	2.21	0.04
PROPIONITRILE	-6.5	0.9	3.7	0.3	2.8	4.01	-0.01
MA	-6.9	1.1	4.0	0.2	2.9	1.26	-0.03
Sulfur donor solvents							
NMPT	-5.9	-0.4	2.7	0.4	3.1	4.90	0.35
DMTF	-6.1	-0.6	2.7	0.4	3.4	4.84	0.25
THIOUREA	-6.0	0.3	3.1	0.3	2.9	5.25	0.42
Halides							
I-	-0.2	14.0	7.1	0.1	-6.9		
Br-	0.4	16.3	7.9	0.1	-8.4		
Cl-	1.2	21.7	10.2	0.0	-11.5		

Table S42: Chemical properties of solvents including: HOMO, LUMO, hardness (η), softness ($1/\eta$), and electronegativity (χ) all in units of eV, along with the dipole moment (μ) and UMBO of the solvent molecules determined via DFT.

Lewis acid	HOMO	LUMO	η	$1/\eta$	χ
BF ₃	-12.6	-1.0	5.8	0.17	6.8
PbI_2	-7.2	-3.2	2.0	0.50	5.2
PbBr ₂	-7.9	-3.2	2.3	0.43	5.5
PbCl ₂	-8.1	-3.0	2.6	0.39	5.5
SnI_2	-7.1	-3.2	2.0	0.51	5.2
SnBr ₂	-7.6	-3.2	2.2	0.45	5.4
$SnCl_2$	-8.1	-3.1	2.5	0.40	5.6
GeI ₂	-6.9	-3.0	2.0	0.51	5.0
GeBr ₂	-7.8	-3.1	2.4	0.42	5.5
GeCl ₂	-8.2	-3.0	2.6	0.39	5.6
BiI ₃	-7.1	-2.2	2.4	0.41	4.6
BiBr ₃	-8.3	-2.6	2.8	0.35	5.5
BiCl ₃	-8.8	-2.2	3.3	0.30	5.5
SbI ₃	-7.1	-2.1	2.5	0.40	4.6
SbBr ₃	-8.3	-2.3	3.0	0.33	5.3
SbCl ₃	-8.8	-2.0	3.4	0.30	5.4
SnI ₄	-8.0	-4.1	2.0	0.51	6.0
SnBr ₄	-9.0	-3.4	2.8	0.36	6.2
SnCl ₄	-9.8	-3.2	3.3	0.30	6.5
SbI ₅	-7.0	-3.4	1.8	0.56	5.2
SbBr ₅	-8.4	-4.8	1.8	0.55	6.6
SbCl ₅	-9.3	-4.4	2.4	0.41	6.9
Li^+	-65.4	-6.1	29.6	0.03	35.8
Na ⁺	-40.6	-6.5	17.1	0.06	23.6
K^+	-27.6	-5.5	11.1	0.09	16.6
Rb^+	-23.5	-5.5	9.0	0.11	14.5
Cs^+	-20.2	-5.1	7.6	0.13	12.7

Table S43: Chemical properties of perovskite Lewis acids, including: HOMO, LUMO, hardness (η), softness ($1/\eta$), and electronegativity (χ) all in units of eV.

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