Electronic Supplementary Material (ESI) for CrystEngComm.

Structural Trends in Hybrid Perovskites, $[Me_2NH_2]\ M\ [HCOO]_3$ (M=Mn, Fe, Co, Ni, Zn). Computational Assessment Based on Bader Charge Analysis.

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Electronic Supplementary Information, ESI

ST1. Computed and experimental volumes *__normalized per 1 formula unit__*, [Me_2NH_2] M [$HCOO$]$_3$

M	Exp.	U=2	U=4	U=6	Average computed Volume
Mn	229.5	229.4	230.5	231.2	230.3
Fe	221.0	221.3	222.3	222.3	222.0
Co	215.6	215.3	216.1	216.6	216.0
Ni	215.6	209.4	209.8	210.5	209.9
Zn	215.8	216.5	214.9	213.0	214.8

ST2. The FFT grids used for Bader analysis.

M	NGXF	NGYF	NGZF
Mn	100	98	98
Fe	100	98	98
Co	98	96	96
Ni	100	100	100
Zn	98	96	96

ST3. Computed Bader charges (a) and volumes (b) of the metal atoms, M, in each system:

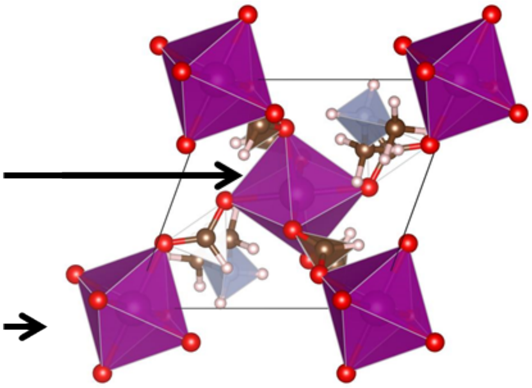
(a)

M	U=2	U=4
Mn	1.53	1.54
Fe	1.46	1.47
Co	1.34	1.36
Ni	1.27	1.30
Zn	1.36	1.35

(b)

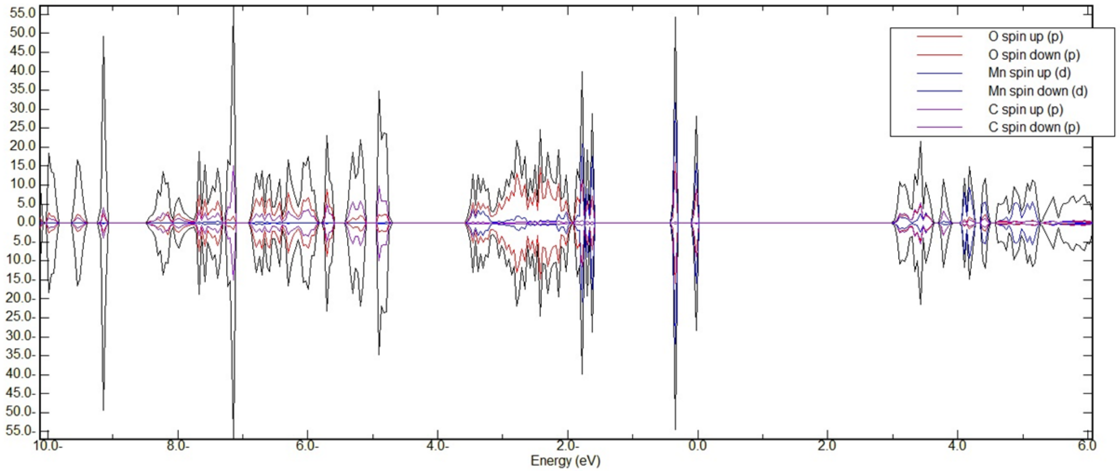
M	U=2	U=4
Mn	10.87	10.86
Fe	10.37	10.37
Co	10.09	10.05
Ni	9.71	9.62
Zn	9.67	9.52

SF1. Rhombohedric simulation cell, 48 atoms, 2 formula units. The metal centers (violet octahedra) of each of the formula units are indicated with arrows. Other violet octahedra represent the periodic images. Red, brown and white spheres indicate oxygen, carbon and hydrogen atoms. The nitrogen atoms are within the blue tetrahedra.

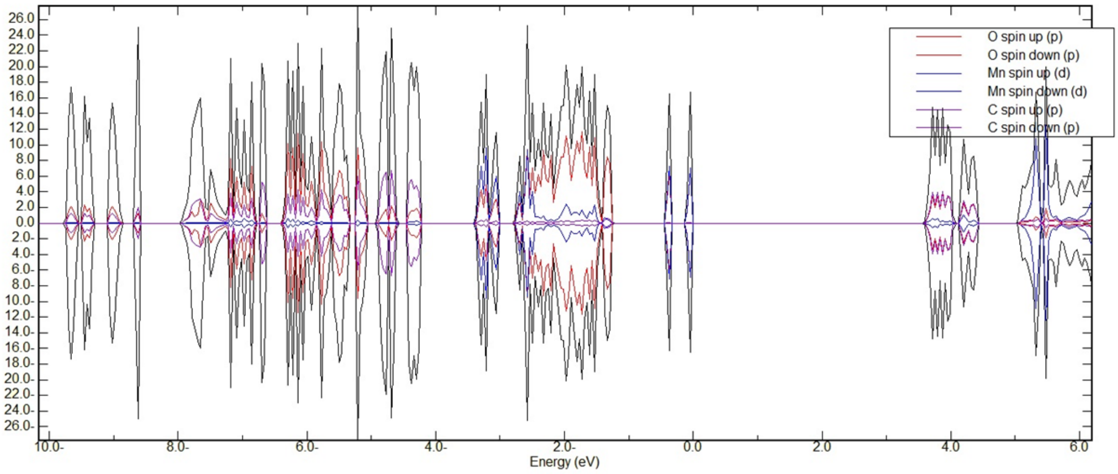


SF2. Electronic Density of States (DOS) of $[Me_2NH_2]\ M\ [HCOO]_3$ as function of U.

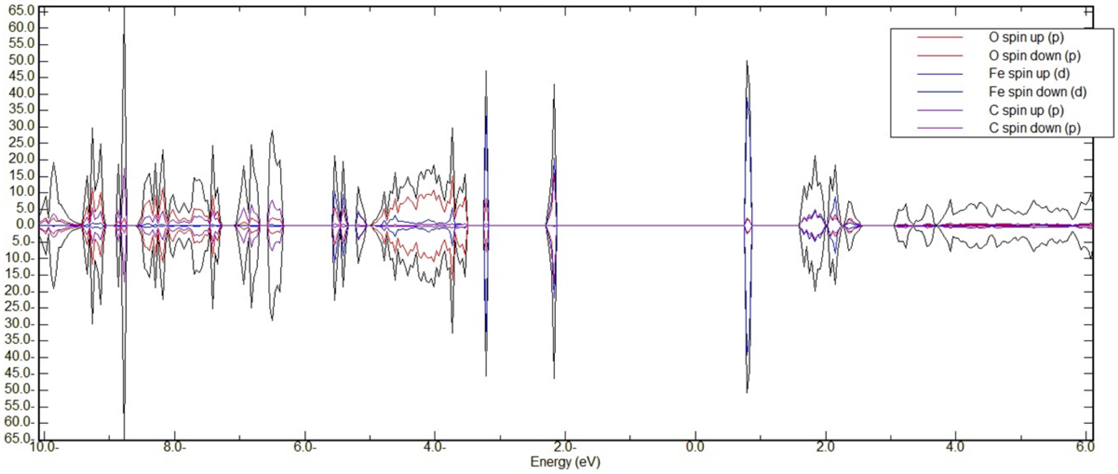
M=Mn, U=2



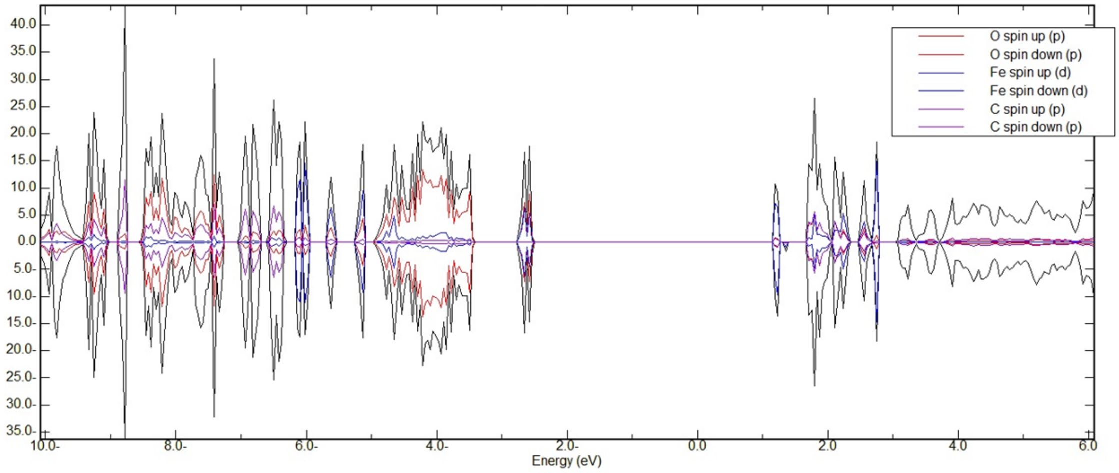
M=Mn, U=4



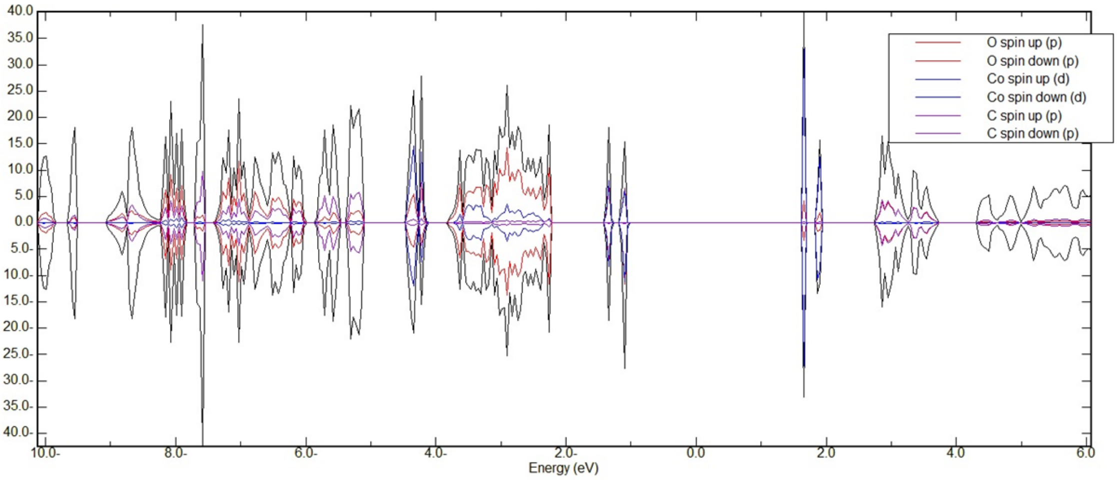
M=Fe, U=2



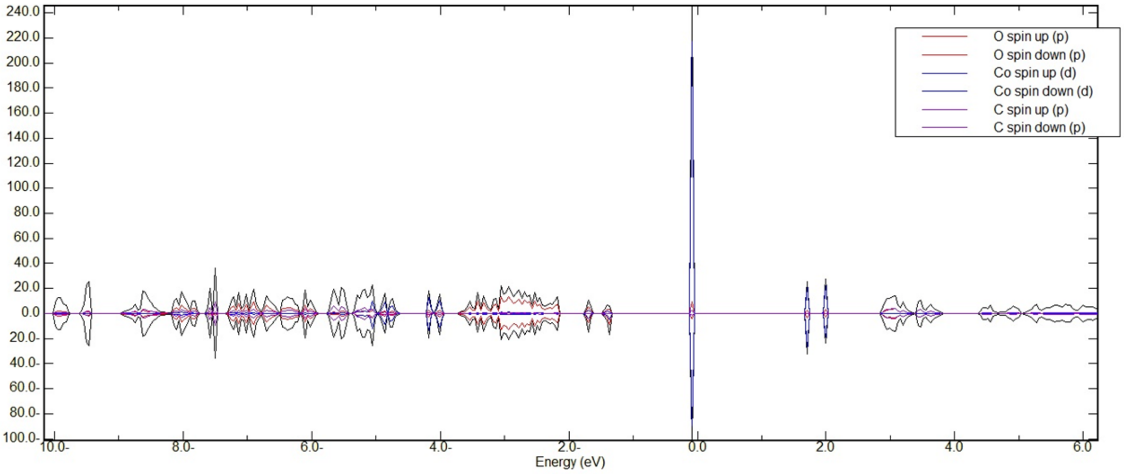
M=Fe, U=4



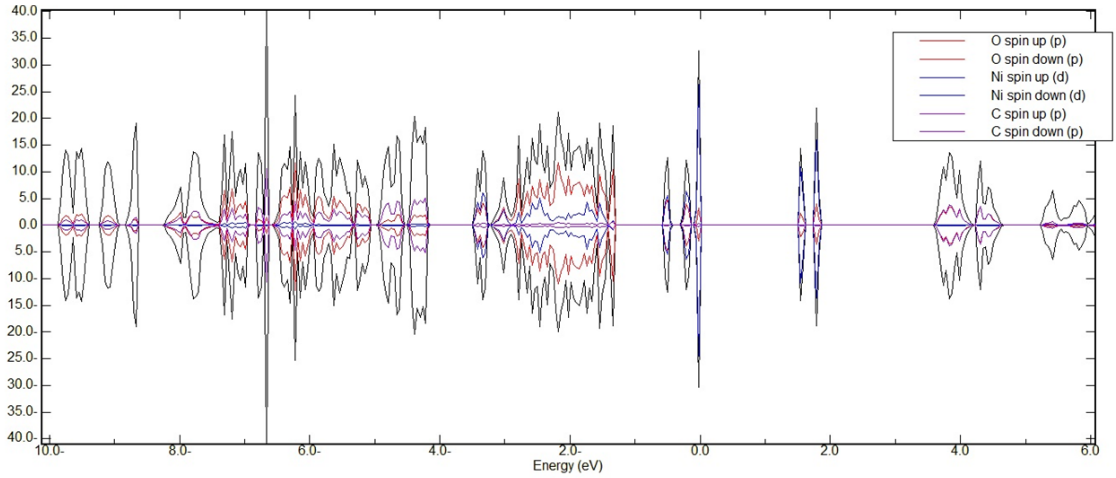
M=Co, U=2



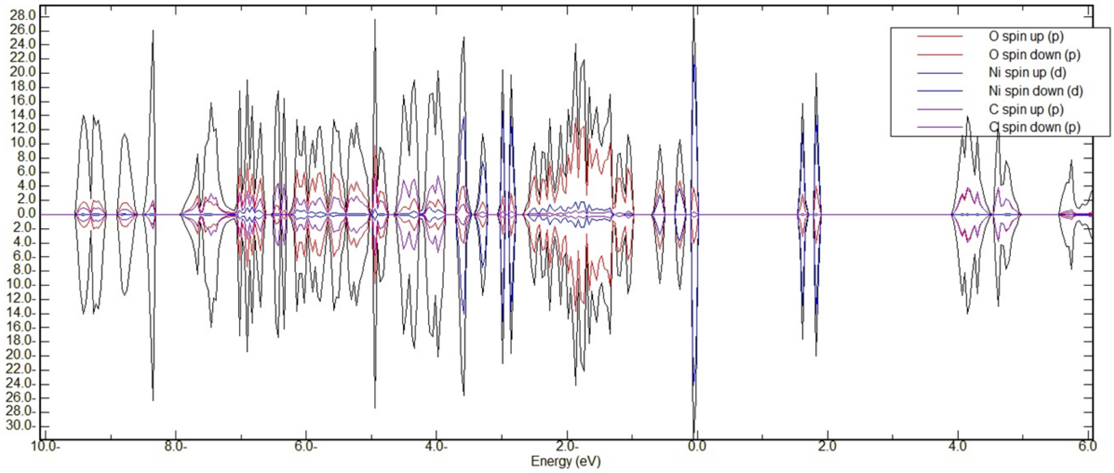
M=Co, U=4



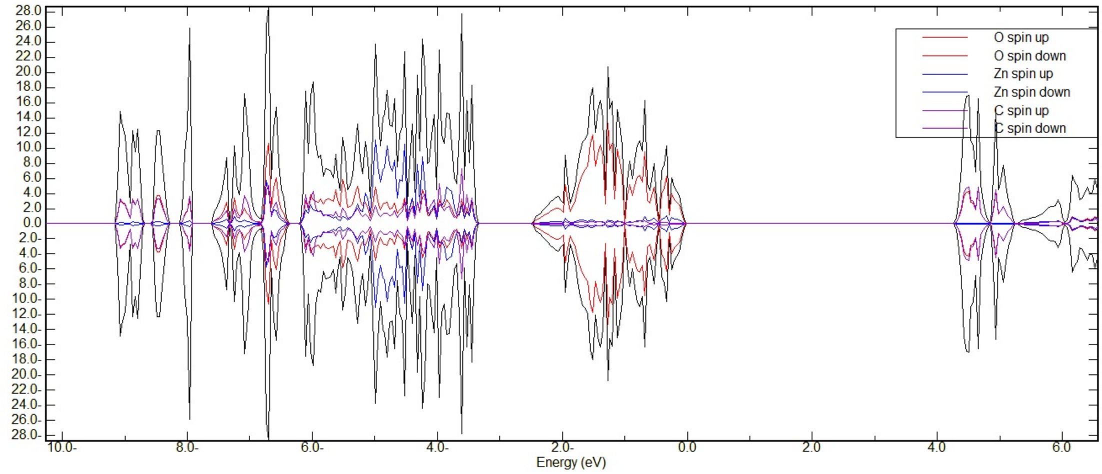
M=Ni, U=2



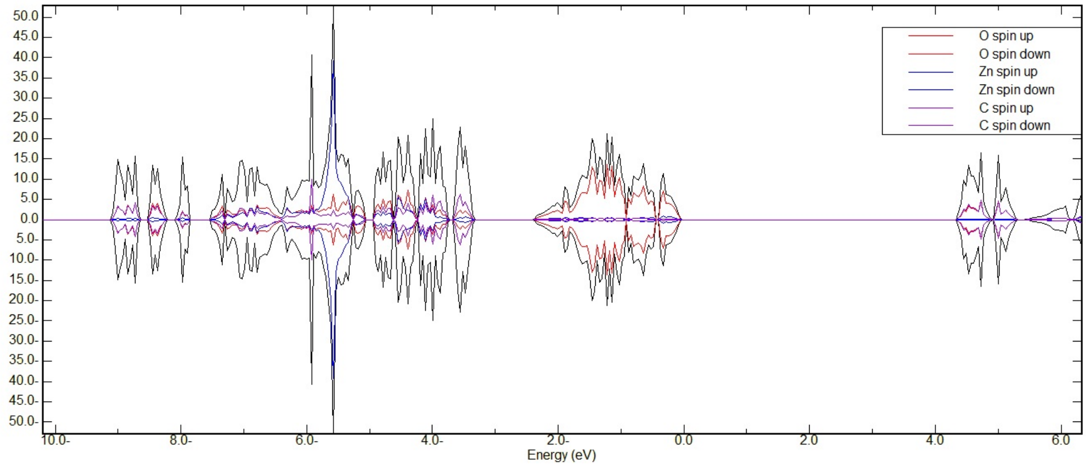
M=Ni, U=4



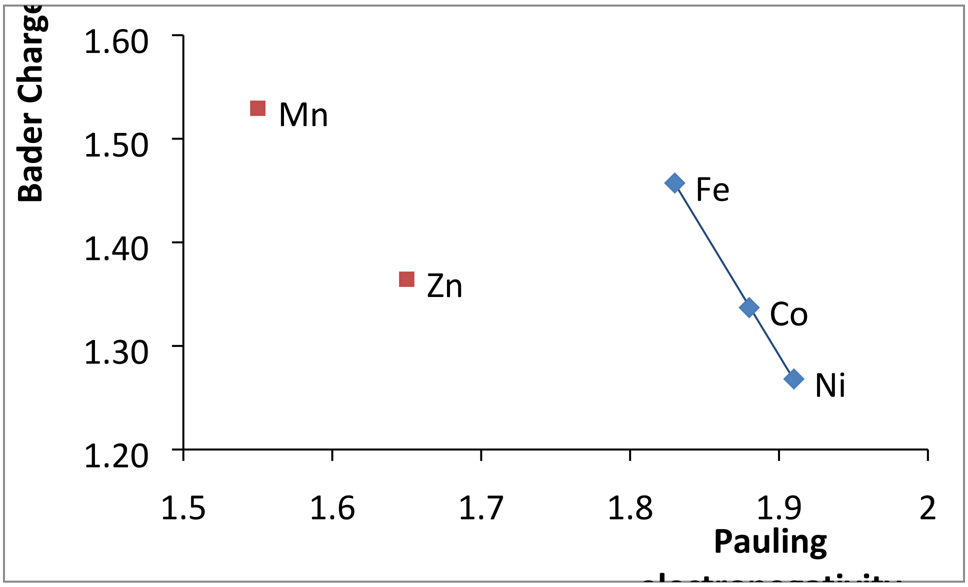
M=Zn, U=2



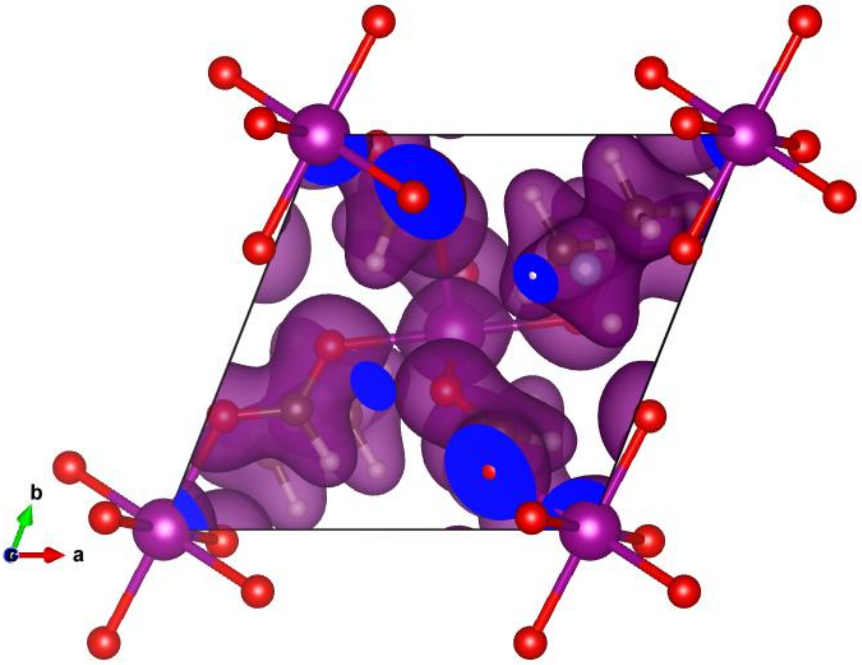
M=Zn, U=4

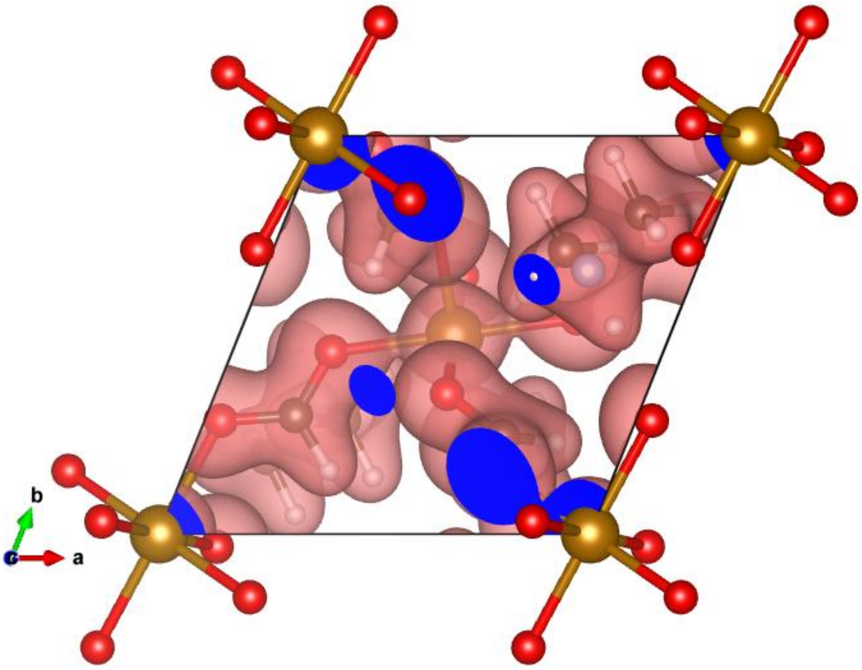


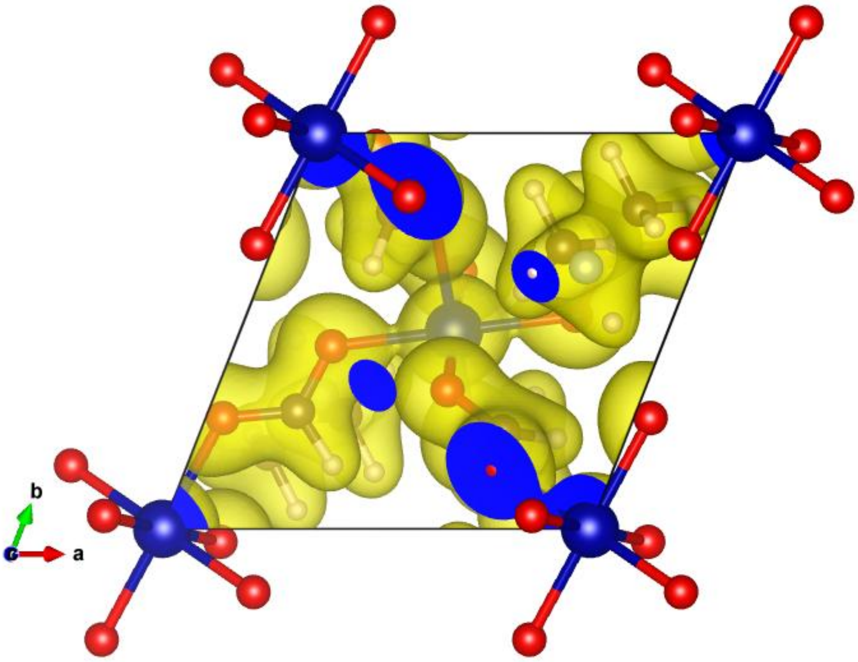
SF3. Correlation of Pauling electronegativity and Bader charges of the metal atoms, M, in $[Me_2NH_2]$ M $[HCOO]_3$.

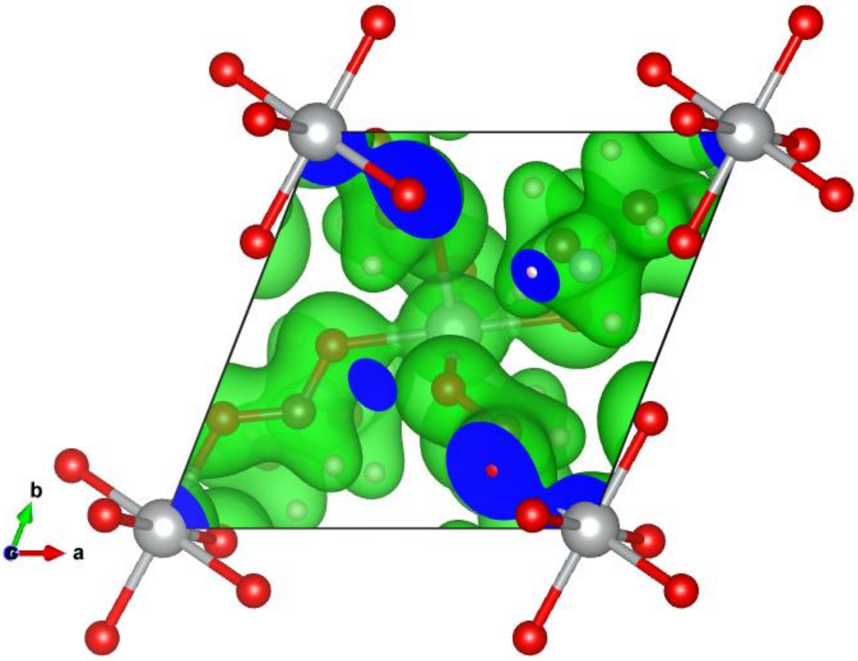


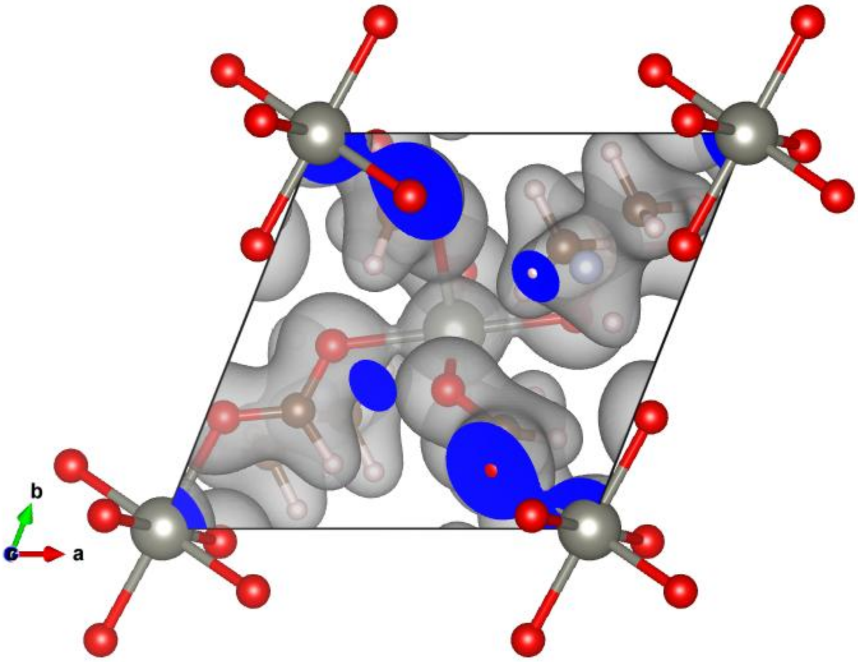
SF4. $0.055a_0^{-3}$ isodensity surface (a_0: Bohr radius): Mn(purple), Fe(pink-red), Co(yellow), Ni(green), Zn(gray)


b
a


b
a


b
c
a


b
c
a


b
c
a

Evaluation of the electrostatic interaction between the metal formate anionic framework and the dimethylammonium cation.

In an attempt to further understand the bonding interactions in hybrid perovskites we have analyzed the electrostatic interaction between the positive dimethylammonium cation and the metal formate negative framework as follows:
After optimizing the systems, as described in the "Computational methods" section in the main text, single point energy calculations were performed for the negative metal formate framework, with a neutralizing background charge of +1 and the positive dimethyammonium cation with the neutralizing background charge of -1. The energetic contribution, ΔE, was computed according to the following equation:

$[Me_2NH_2]^+ + [MHCOO]^-_3 \rightarrow [Me_2NH_2]\,M\,[HCOO]_3$ (ΔE)

The M=Mn was taken as a reference

M	ΔE, kJ/mol, per 1 formula unit
Mn	0.00
Fe	-7.90
Co	-12.12
Ni	-21.38
Zn	+7.32

The electrostatic interaction increases from Mn to Ni (with increasing negative interaction energies) and decrease for Zn. It is consistent with the decreasing cell parameters for Mn, Fe, Co, Ni and small variation in the computed Bader charges of the dimethylamonium cation (and its formal charge of +1). Despite the correct qualitative trend, the quantitative isolation and assessment of the bonding of the dimethylammonium and the metal formate framework might be challenging due to the hydrogen bonds between the dimmethylammonium and the oxygens of the formate ligands.