SUPPLEMENTARY MATERIAL

Charge Localisation in Heavy Alkali Metal Ion Complexes of 4,4'-Biphenyldicarboxylate

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Figure S1

(a) Distribution of biphenyl-twist dihedral angles in the 22816 structures in the CSD containing the biphenyl unit with a wide variety of substituents:

(b) Distribution of the dihedral angles in biphenyl systems with substituents in the 4- or 4,4' positions only:
Figure S2  (i) Eight-coordinate Cs(I) and (ii) five-coordinate O in anhydrous CsO$_2$CCH$_3$.$^{25}$

Carboxylate C-O 1.240(10), 1.270(6) Å.
Figure S3  Carboxylate coordination arrays in:

(a) Caesium chelidamate, $\text{Cs}_2\text{C}_7\text{H}_3\text{NO}_5$

(b) Rubidium chelidamate, $\text{Rb}_3(\text{C}_7\text{H}_3\text{NO}_5)(\text{C}_7\text{H}_4\text{NO}_5).6\text{H}_2\text{O}$
(c) Lithium chelidamate, \( \text{Li}_2\text{C}_7\text{H}_3\text{NO}_5\cdot3\text{H}_2\text{O} \)
Figure S4  Carboxylate coordination arrays in :

(a) Sodium 2,2'-bipyridine-3,3'-bicarboxylate tetrahydrate (isomorphous with the potassium analogue)

(b) Rubidium 2,2'-bipyridine-3,3'-bicarboxylate monohydrate (isomorphous with the caesium analogue)