1,1`-Fc(*para*-$C_6H_4CO_2Et)_2$ and its unusual salt derivative with *Z*'=5, *catena*-$[Na^+]_2$[1,1`-Fc(*para*-$C_6H_4CO_2^-)_2$]:(3/5)H_2O, {1,1`-Fc = $?^5(C_5H_4)_2Fe$}

John F. Gallagher[*a], Steven Alley[a], Marianne Brosnan[a] and Alan J. Lough[b]

[a] School of Chemical Sciences, Dublin City University, Dublin 9, Ireland, and
[b]Department of Chemistry, 80 St. George Street, University of Toronto, Toronto, Ontario, Canada M5S 3H6

Correspondence e-mail: john.gallagher@dcu.ie

Synopsis

The neutral 1,1'-bis{ethyl(*para*-benzoate}ferrocene, 1,1'-Fc(*para*-$C_6H_4CO_2Et)_2$, {1,1`-Fc = $?^5(C_5H_4)_2Fe$} yields the complex salt with Z'=5, *catena*-$[Na^+]_2[?^5(C_5H_4)_2Fe$(*para*-$C_6H_4CO_2^-)_2$]:(3/5)H_2O, crystallized with difficulty as small red crystals over four weeks from a water/dimethylformamide/pyridine (2:2:1) solution. The asymmetric unit as *catena*-$[Na^+]_{10}[?^5(C_5H_4)_2Fe$(*para*-$C_6H_4CO_2^-)_2]_5$:$3H_2O$, comprises five dianions stacked in a ladder-type arrangement about a central 2-D layer of ten Na^+ ions and three water molecules, with units linked by ionic bonds and O—H···O interactions. The five dianions differ in their *cisoid* conformations with distortions in the pendent benzenecarboxylate groups.

Supplementary Materials

The Supplementary materials contain some additional diagrams and tables compiled to assist further in the understanding of the structures of (I) and (II).

Supplementary Figure legends S1-S6 (pages 3 – 13 below):

Figure_S1. A stereoview of the molecular packing in (I) with atoms depicted as their van der Waals spheres.

Figure_S2. The five dianions and three water molecules in the asymmetric unit and highlighting the distorted nature of dianions (C) and (E). Displacement ellipsoids are depicted at the 30% probability level. The Na^+ cations are omitted for clarity to showcase the dianion packing and hydrogen bonding.

Figures_S3a-c. Views of the unit cell along the [010], [100] and [001] directions and the one-dimensional chain of water molecules generated along the *b* axis direction.

Figures_S4a-c. Views of the unit cell along the [010], [100] and [001] directions and the one-dimensional chain of water molecules and Na^+ columns generated along the *b* axis direction.

Figure_S5a,b. Views of the coordination geometry of Na6 and Na8 with the atomic numbering scheme: displacement ellipsoids are at the 30% level. The symmetry operations are \$ = 1 - *x*,-1/2 + *y*,1/2 - *z*, * = - 1/2 + *x*,*y*,1/2 - *z* and & = 1 - *x*,1/2 + *y*,1/2 - *z*.

Figure_S6. A view of two of the C—H···p(arene) interactions in (II) with atoms depicted as their van der Waals spheres. The molecules represented by & and # are located at the symmetry positions 1 - *x*,1/2 + *y*,1/2 - *z* and 3/2 - *x*,1/2 + *y*,1/2 - *z*.

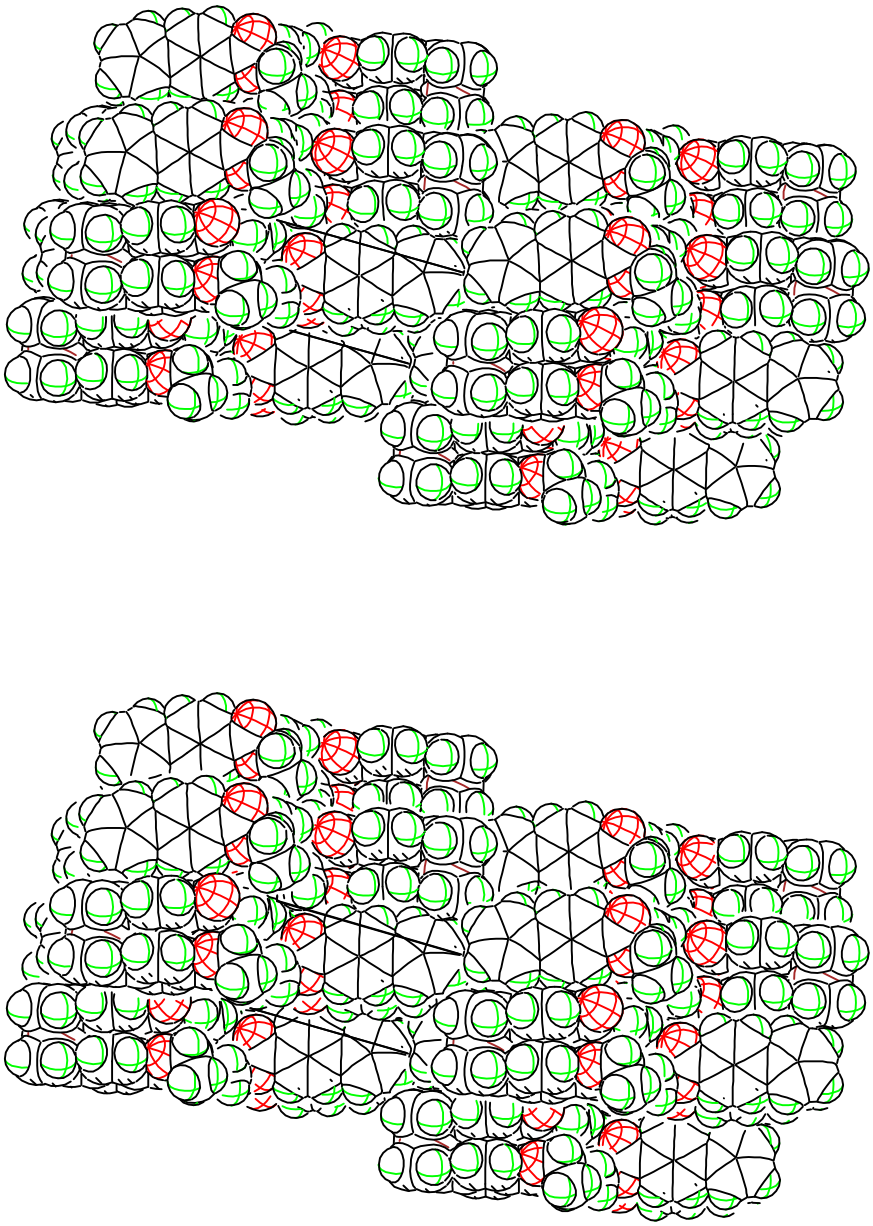
<u>Supplementary Tables 1-3</u>

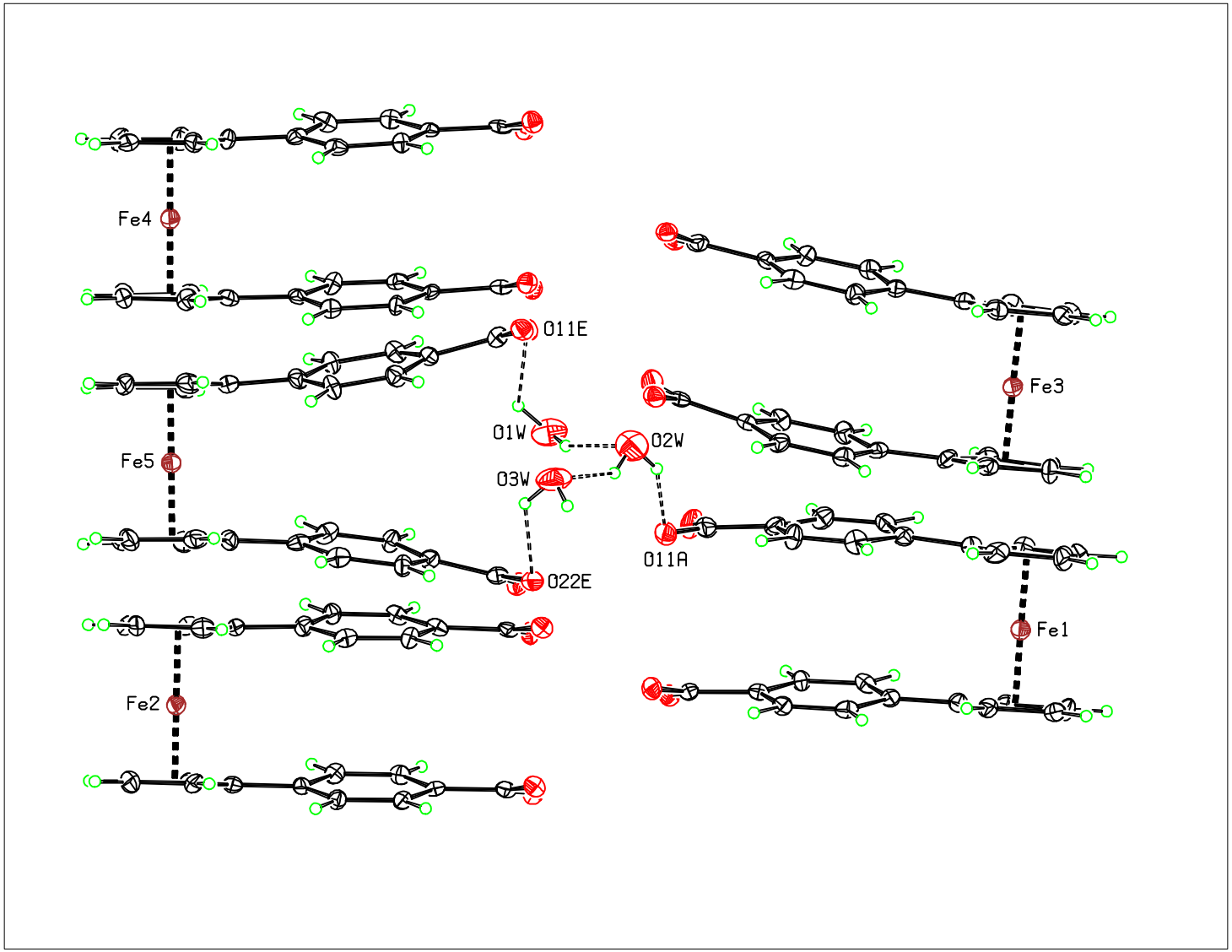
Table 1 details the interaction and contact geometry in (I).

Interaction and contact geometry in (I) (Å, °).

Tables 2 and 3 show the six shortest Na…O distances and spread of Na…O distances together with the carboxylate chelate angle and O-Na-O basal angles in (II).

Coordination geometry of the ten Na^+ cations in (II): Na···O distances[a] (Å).
Coordination geometry of the ten Na^+ cations in (II): geometry details for the carboxylate CO_2 bite[i] and *trans* O···Na···O basal angles (°).

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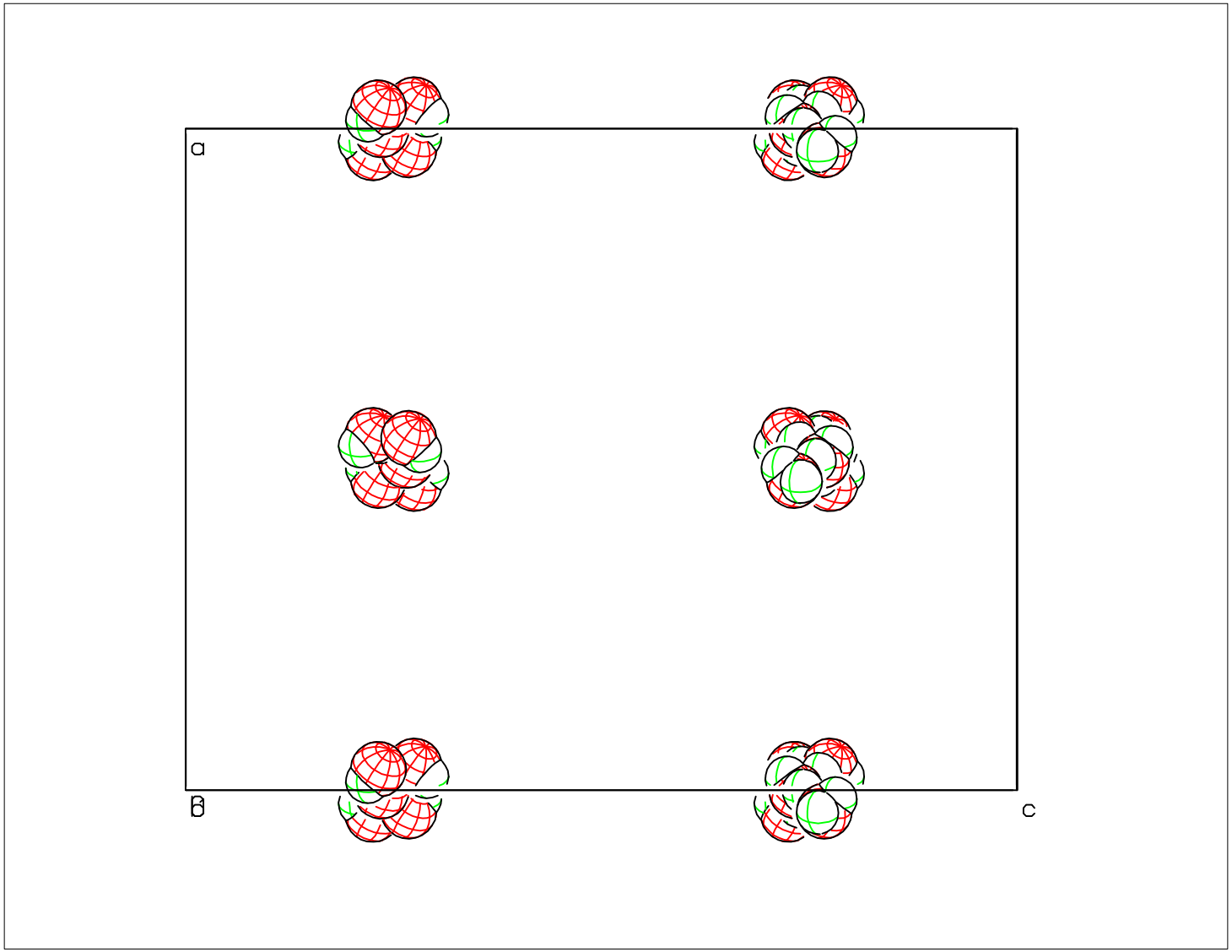
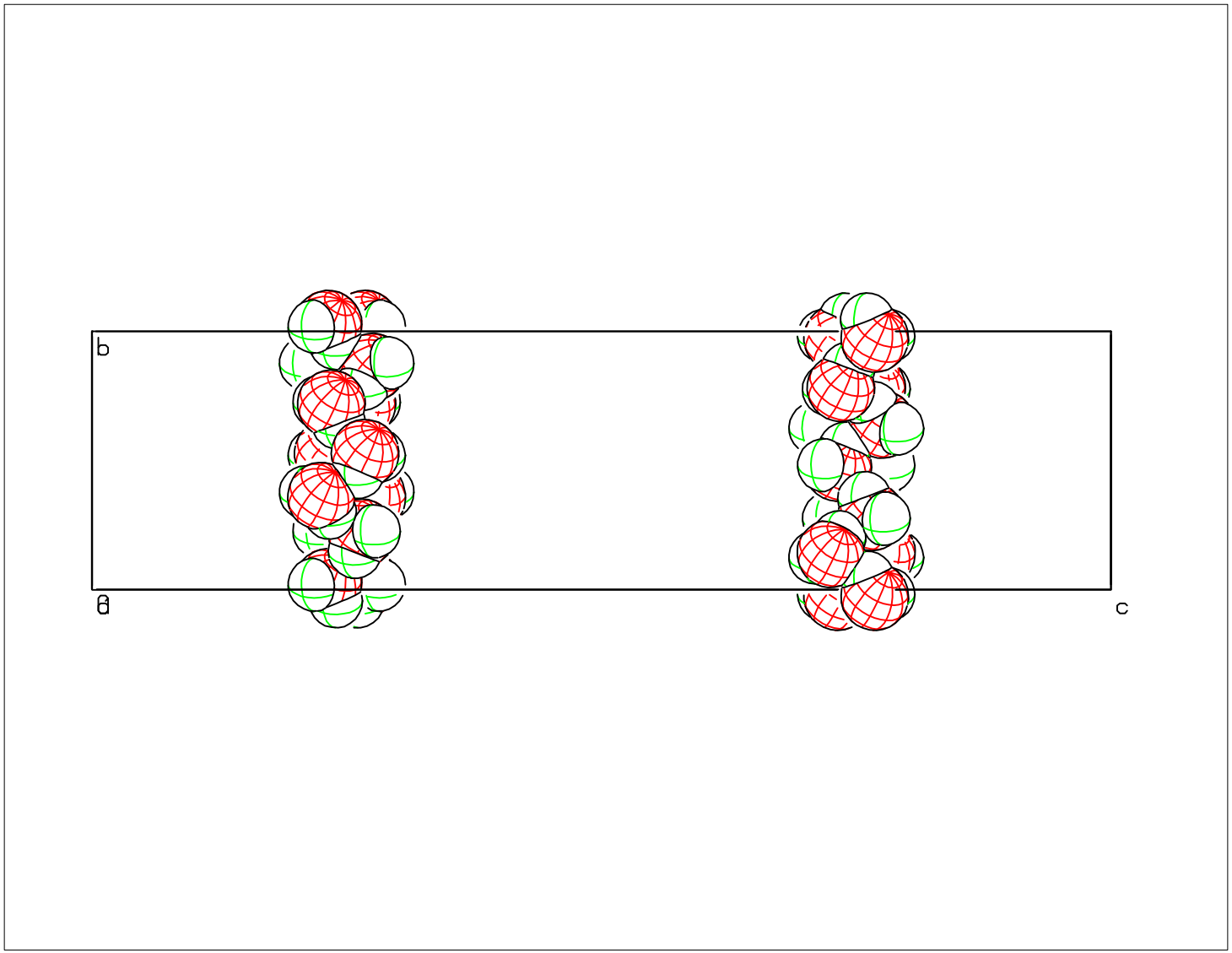

a
b
c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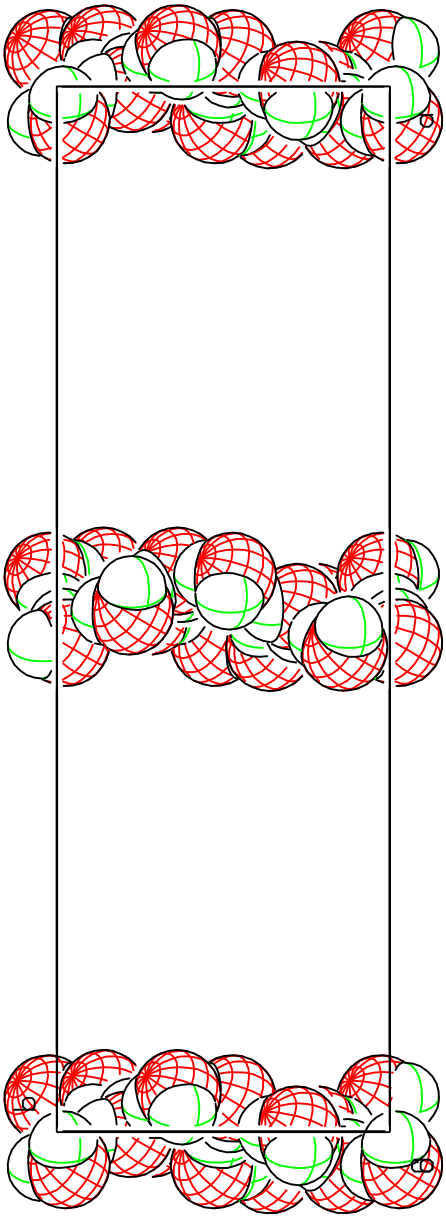

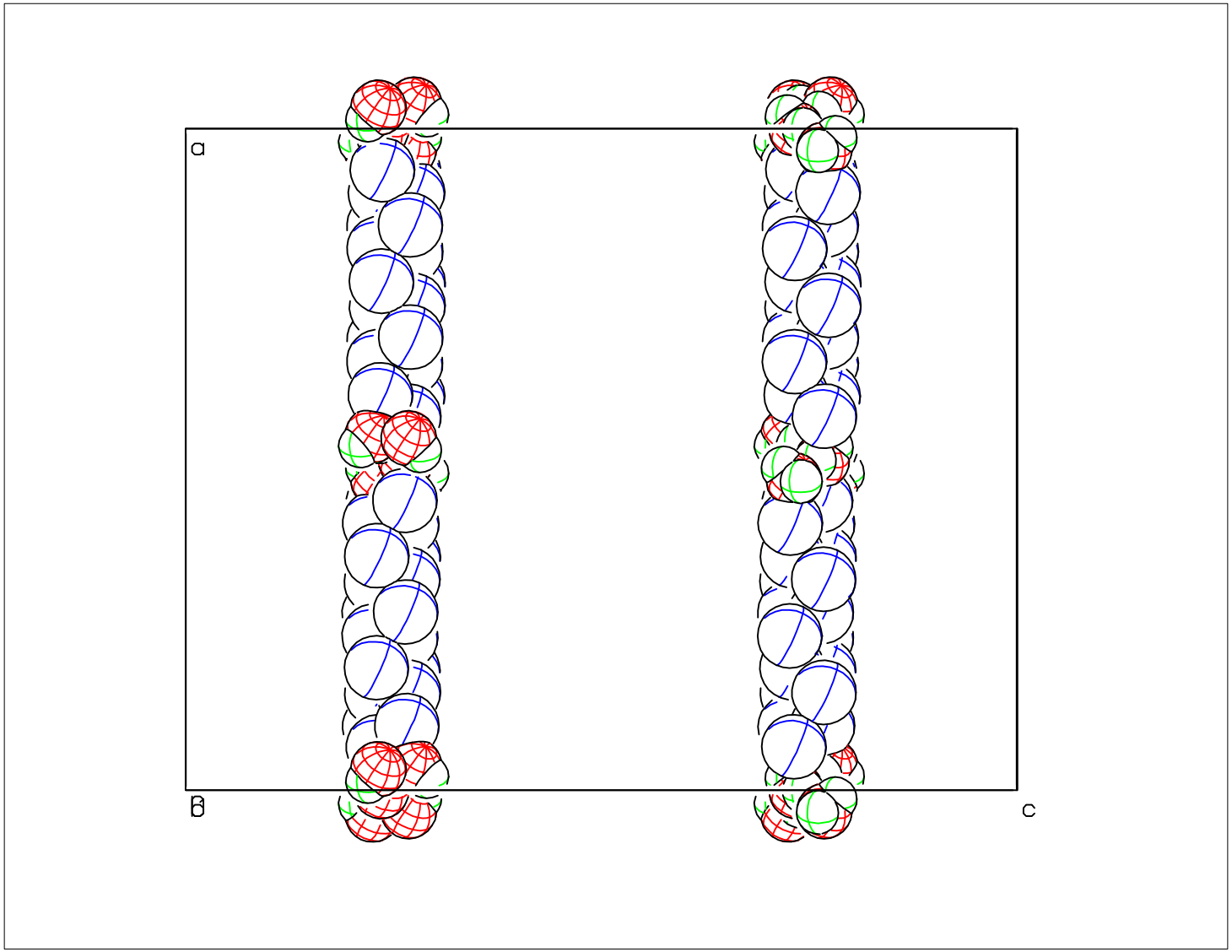
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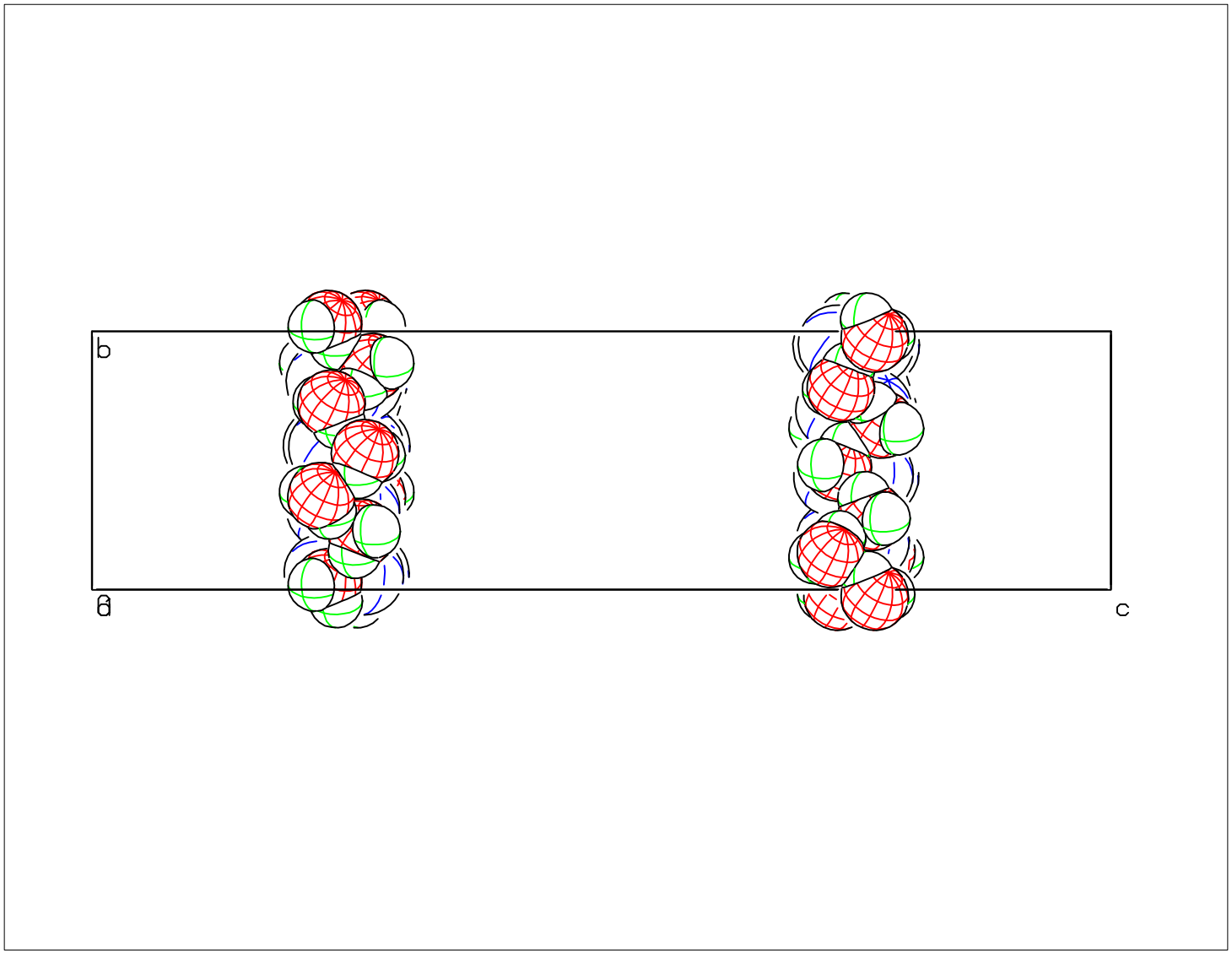
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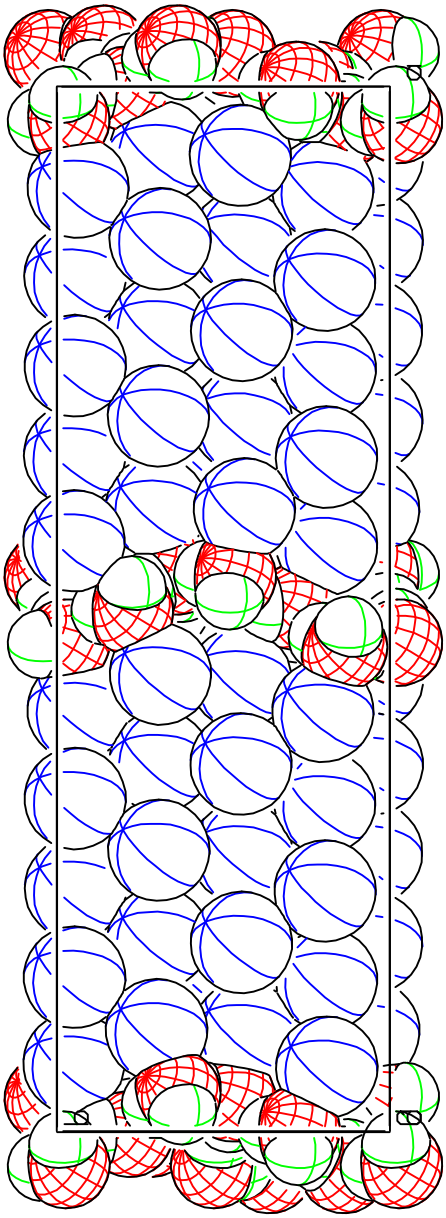
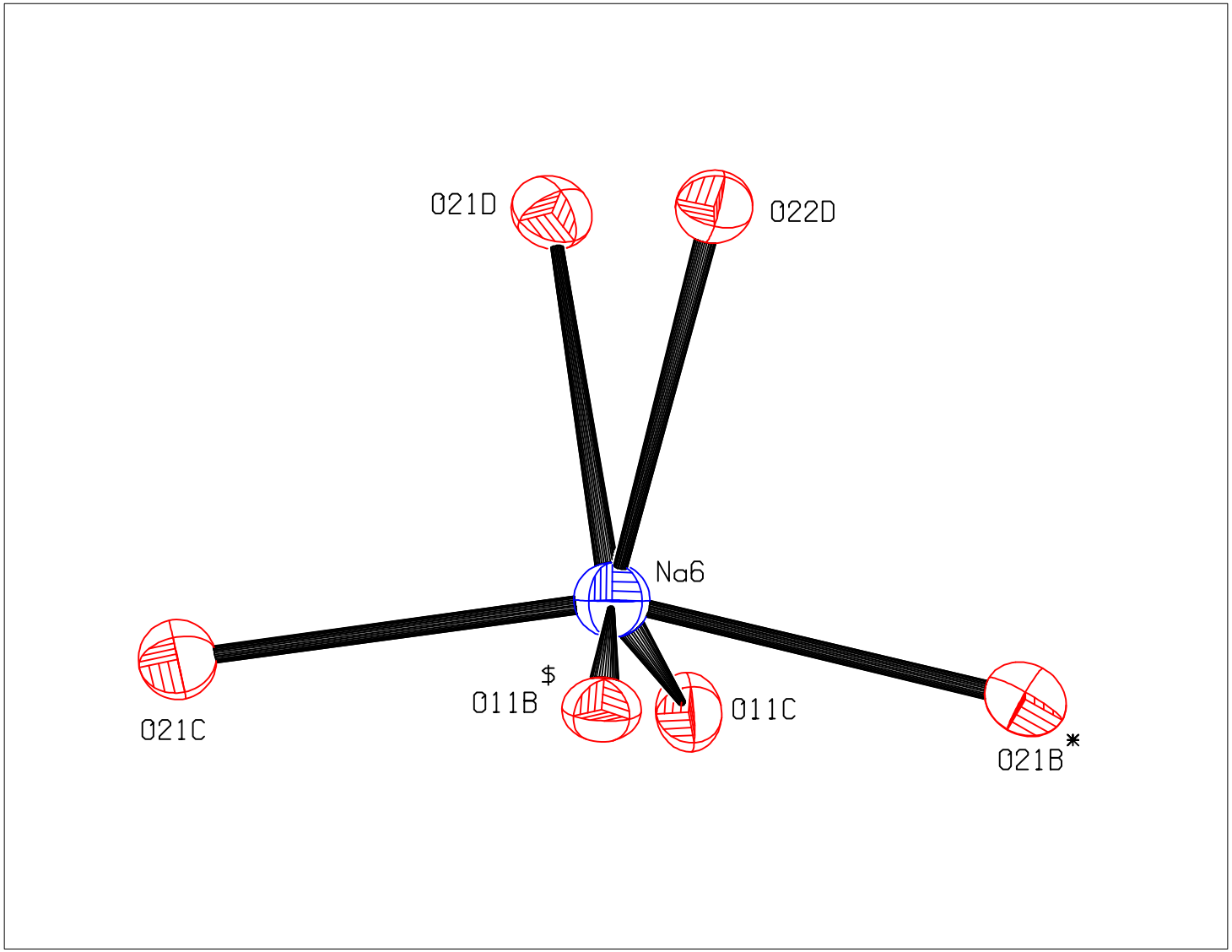
c

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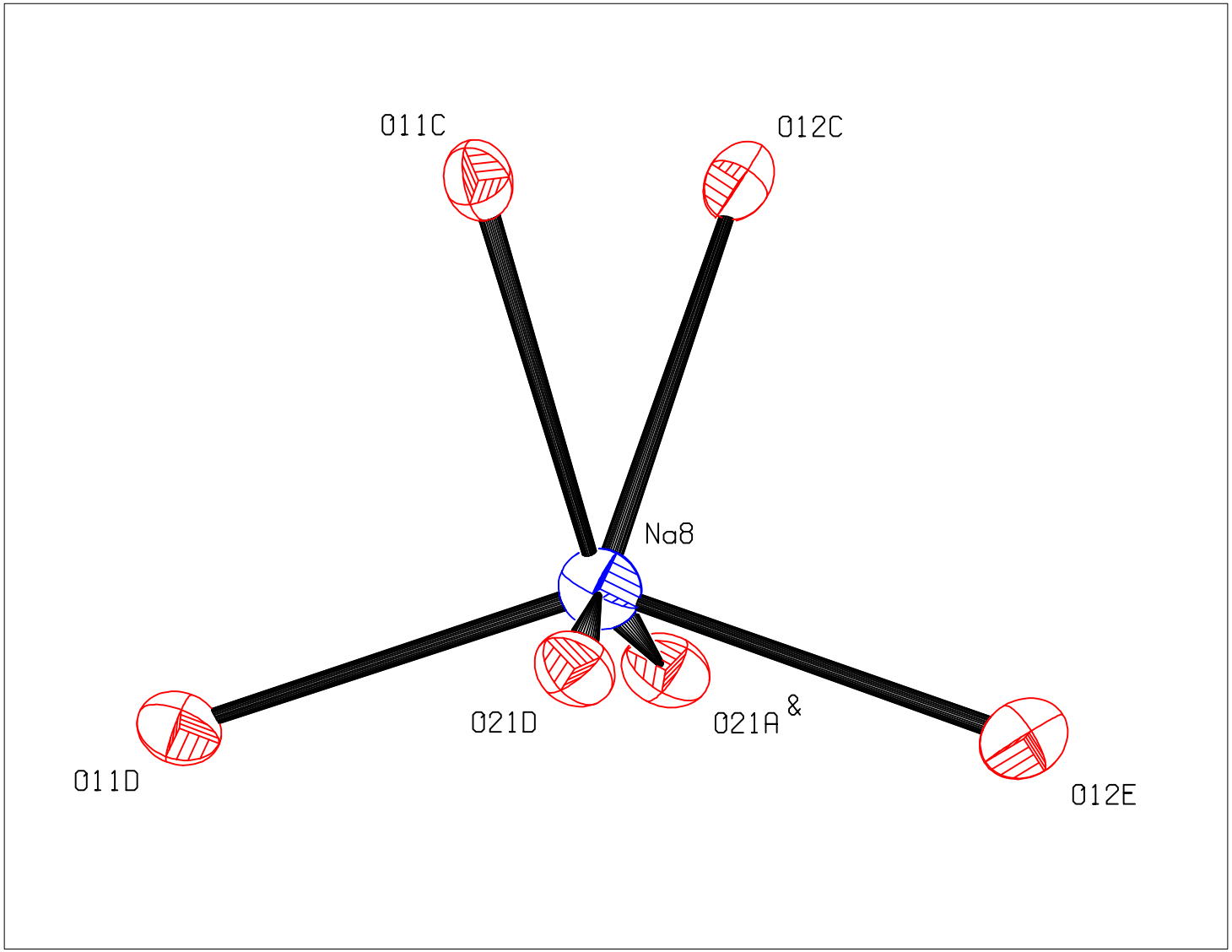
022D
Na6
021C
011B$
011C
021B*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Na8
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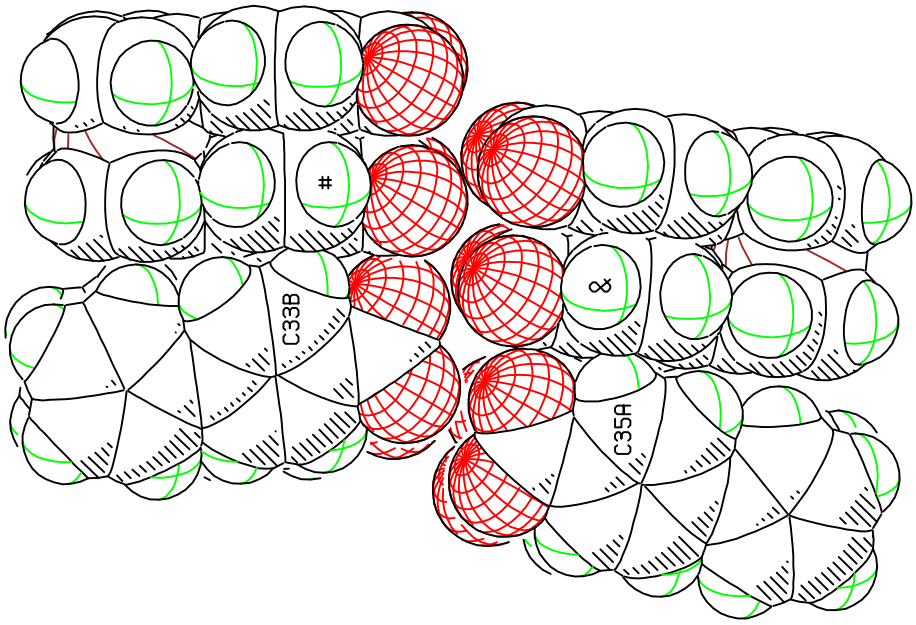
O21A
&
O11D
O12E


#
C33B
&
C35A

Supplementary Table 1

Interaction and contact geometry in (I) (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C6A—H6A2···O3B^{i}	0.98	2.69	3.613 (4)	156
C35A—H35A···O1B^{ii}	0.95	2.64	3.504 (4)	151
C15B—H15B···C32A^{iii}	0.95	2.72	3.667 (4)	171
C33B—H33B···O1A^{iii}	0.95	2.63	3.476 (4)	148

Symmetry codes: (i) -*x*+1, -*y*+1, -*z*; (ii) *x*+1, *y*-1, *z*; (iii) *x*, *y*+1, *z*.

Supplementary Table 2

Coordination geometry of the ten Na^+ cations in (II): Na···O distances[a] (Å)

Na^+	Na···O	Na···O	Na···O	Na···O	Na···O	Na···O	? range
Na1	2.226 (5)	2.285 (5)	2.349 (5)	2.351 (5)	2.673 (4)	3.131 (6)[b]	0.90
Na2	2.318 (5)	2.339 (5)	2.380 (5)[b]	2.397 (5)	2.438 (5)	2.815 (5)	0.50
Na3	2.302 (5)	2.355 (5)	2.368 (4)	2.402 (5)	2.544 (5)	2.719 (4)	0.42
Na4	2.246 (5)	2.326 (5)	2.404 (4)	2.419 (5)	2.665 (4)	2.979 (5)	0.73
Na5	2.339 (5)	2.412 (5)	2.433 (4)	2.446 (5)	2.492 (5)	2.549 (4)	0.21[c]
Na6	2.339 (5)	2.406 (5)	2.432 (5)	2.479 (4)	2.501 (4)	2.502 (5)	0.16[c]
Na7	2.278 (5)	2.345 (5)	2.422 (5)	2.464 (4)	2.594 (5)	2.701 (4)	0.42
Na8	2.284 (5)	2.332 (5)	2.525 (5)	2.528 (4)	2.552 (5)	2.570 (4)	0.29
Na9	2.201 (5)	2.306 (5)	2.442 (5)[b]	2.472 (5)	2.519 (4)	2.610 (5)	0.41
Na10	2.347 (5)	2.352 (5)	2.372 (5)	2.390 (5)[b]	2.415 (5)	2.623 (5)	0.28

Notes: (*a*) The six shortest Na^+···O distances are listed for each of the ten Na^+ ions. (*b*) The Na^+···O distance involves a water molecule. (*c*) The smallest Na^+···O distance ranges are for Na5 and Na6, the largest for Na1 and Na4.

Supplementary Table 3

Coordination geometry of the ten Na^+ cations in (II): geometry details for the carboxylate CO_2 bite[i] and *trans* O···Na···O basal angles (°)

Na^+	Cxn[i]	CO_2···Na^{ii}	O···Na···O[iii]	O···Na···O[iii]
Na1	C2E	51.82 (14)	138.42 (19)	155.13 (18)[iv]
Na2	C1A	49.36 (14)	142.88 (17)	158.9 (2)[iv]
Na3	C2A	51.23 (14)	153.87 (17)	154.54 (15)
Na4	C1B	51.94 (14)	147.18 (15)	149.84 (17)
Na5	C2B	52.78 (14)	149.00 (17)	158.01 (16)
Na6	C2D	52.80 (14)	147.64 (16)	158.68 (16)
Na7	C1D	50.81 (13)	145.43 (16)	154.62 (17)
Na8	C1C	51.69 (13)	142.62 (15)	156.71 (17)
Na9	C1E	51.52 (13)	150.79 (18)	158.3 (2)[iv]
Na10	C2C	52.20 (15)	142.68 (17)	172.0 (2)[iv]

Notes: (i) The carboxylate group chelating Na^+ (with x = 1 or 2, n = A to E). (ii) The carboxylate O-C-O chelate angle at Na^+. (iii) The two basal *trans* O···Na···O angles. (iv) Geometry involving one water molecule.