

Sesquicaesium hemisodium tetra-cyanidoplatinate(II) sesquihydrate

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Key indicators: single-crystal X-ray study; $T = 290$ K; mean $\sigma(\text{N}-\text{C}) = 0.008$ Å; R factor = 0.014; wR factor = 0.034; data-to-parameter ratio = 15.5.

The title compound, $\text{Cs}_{1.5}\text{Na}_{0.5}[\text{Pt}(\text{CN})_4]\cdot 1.5\text{H}_2\text{O}$, was isolated from solution as a salt. The tetracyanidoplatinate (TCP) anions are stacked in a linear quasi-one-dimensional arrangement along the b axis, with Pt··Pt interactions of 3.6321 (5) Å. The mixed alkali metal TCP contains three distinct alkali metal positions in the structure that do not show any mixed occupancy: Cs1 (site symmetry 2), Cs2 (general position) and Na1 (site symmetry $\bar{1}$). The Na^+ ion contains an octahedral coordination environment composed of two water molecules and four N-terminal cyanides, which serve to bridge TCP anions. The Cs^+ cations contain mono- and biccapped square-prismatic environments, where the square prisms are formed from cyanide N atoms with water molecules capping the faces. The 1.5 water molecules per formula unit are a result of two fully occupied sites, one on a general position and one on a twofold rotation axis. Weak hydrogen-bonding interactions are observed between one water molecule and terminal N-atom acceptors from TCP, while the second water molecule is not involved in hydrogen bonding.

Related literature

Crystalline TCP systems have been studied extensively for their interesting structural and spectroscopic, especially photoluminescent, properties (Holzapfel *et al.*, 1981; Gliemann & Yersin, 1985; Stojanovic *et al.*, 2010). An intrinsic factor affecting the optical properties and arrangement of TCP chains is the identity of the cations involved, and much work has been done in the systematic study of various combinations of alkali metal cations involved (Holzapfel *et al.*, 1981). However, only one known reference of a caesium/sodium mixed alkali metal TCP, *viz.* $\text{NaCs}[\text{Pt}(\text{CN})_4]\cdot 1.5\text{H}_2\text{O}$, exists (Bergsoe *et al.*, 1962), which notes the synthesis and scintillation properties for the compound, but not any structural information.

Experimental

Crystal data

$\text{Cs}_{1.5}\text{Na}_{0.5}[\text{Pt}(\text{CN})_4]\cdot 1.5\text{H}_2\text{O}$	$V = 2043.56$ (11) Å ³
$M_r = 1074.11$	$Z = 4$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 17.4090$ (5) Å	$\mu = 18.99$ mm ⁻¹
$b = 7.2190$ (1) Å	$T = 290$ K
$c = 18.3921$ (5) Å	$0.20 \times 0.14 \times 0.08$ mm
$\beta = 117.858$ (4)°	

Data collection

Oxford Diffraction Excalibur-E diffractometer	8164 measured reflections
Absorption correction: multi-scan (<i>CrysAlis PRO</i> ; Oxford Diffraction, 2010)	1949 independent reflections
$T_{\min} = 0.471$, $T_{\max} = 1.00$	1789 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.019$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.014$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.034$	$\Delta\rho_{\text{max}} = 0.63$ e Å ⁻³
$S = 1.15$	$\Delta\rho_{\text{min}} = -0.47$ e Å ⁻³
1949 reflections	
126 parameters	
6 restraints	

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O1}-\text{H1A}\cdots\text{N1}^{\text{i}}$	0.85 (2)	2.37 (3)	3.154 (6)	155 (5)
$\text{O1}-\text{H1B}\cdots\text{N3}^{\text{ii}}$	0.83 (2)	2.17 (2)	2.982 (5)	166 (5)

Symmetry codes: (i) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x, -y + 1, -z$.

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2010); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2385).

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Sesquicaesium hemisodium tetracyanidoplatinate(II) sesquihydrate

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S1. Comment

Crystalline tetracyanidoplatinate (TCP) systems have been studied extensively for their interesting structural and spectroscopic, especially photoluminescent, properties (Holzapfel *et al.*, 1981; Gliemann & Yersin, 1985; Stojanovic *et al.*, 2010). The title compound, $\text{Cs}_{1.5}\text{Na}_{0.5}\text{Pt}(\text{CN})_4 \cdot 1.5\text{H}_2\text{O}$, was obtained as an unexpected product from a reaction that was an attempt to prepare a heterometallic cyanidometalate complex containing Eu(III), TCP, and dicyanidoaurate moieties. A number of related mixed-metal cation (alkali, alkaline-earth) TCPs have been reported (Holzapfel *et al.*, 1981; Gliemann & Yersin, 1985). However, only one known reference of a caesium/ sodium mixed-alkali metal TCP ($\text{NaCsPt}(\text{CN})_4 \cdot 1.5\text{H}_2\text{O}$) exists (Bergsøe *et al.*, 1962), which notes the synthesis and scintillation properties for the compound, but not any structural information.

The structure of the title compound consists of pseudo one-dimensional chains of square-planar TCP anions tethered by Pt...Pt interactions of 3.6321 (5) Å. The platinate chains run parallel to the *b* axis and are bridged by ionic interactions among Cs^+ and Na^+ ions with the N atoms of the cyanidoplatinate, and show a loose packing of water molecules within that space. The water molecules feature weak H-bonding interactions with the N atoms of the platinate as well (Table 1). The Na^+ ion contains a nearly regular octahedral coordination environment composed of two *trans* water molecules and four cyanido N atoms. Cs1 and Cs2 contain mono- and bi-capped square prismatic environments, respectively, where the slightly distorted square prisms are formed from cyanido N atoms and the capping positions are occupied by water molecules. As per each discrete TCP anion, the empirical structure of the compound contains an equivalency of 1.5 Cs^+ as a result of the Cs1 site residing on a twofold rotation axis and Cs2 occupying a general position, 1.5 H_2O molecules due to O1 residing on a general position and the presence of O2 on a twofold rotation axis, and 0.5 Na^+ as a result of Na1 residing on an inversion center.

The N1 and N3 sites, *trans* to one another on the TCP anion, are involved in H-bonding interactions to the water molecule containing O1, while the other *trans* pair of cyanide groups containing N2 and N4 are involved in interactions with Na^+ (2.527 (4) and 2.541 (4) Å, respectively). The O2 water molecule interacts with Cs1 at a distance of 3.103 (6) Å, but does not engage in any meaningful H-bonding interactions.

S2. Experimental

$\text{Eu}(\text{CF}_3\text{SO}_3)_3 \cdot 9\text{H}_2\text{O}$ (98%), $\text{Na}_2\text{Pt}(\text{CN})_4$ (99.95%), $\text{NaAu}(\text{CN})_2$ (99.9%), and CsCl (99.9%) were used as received from Alfa Aesar. The title compound was obtained inadvertently in an attempt to produce a heterometallic cyanidometalate compound containing europium, TCP, and dicyanidoaurate. This involved the following preparation: Eu-trifluoromethanesulfonate (6.0 mg, 0.076 mmol) dissolved in 400 μl 80% $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ within a 5 ml test tube was layered with the solutions of sodium tetracyanidoplatinate (6.9 mg, 0.020 mmol) dissolved in 300 μl 80% $\text{CH}_3\text{CN}:\text{H}_2\text{O}$, and sodium dicyanidoaurate (2.7 mg, 0.010 mmol) dissolved in 400 μl 80% $\text{CH}_3\text{CN}:\text{H}_2\text{O}$. The solution was allowed to stand for 25 minutes until 1 ml caesium chloride (33.7 mg, 0.20 mmol) in 80% $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ solution was layered onto the mixture.

Colorless, transparent crystals of $\text{Cs}_{1.5}\text{Na}_{0.5}\text{Pt}(\text{CN})_4 \cdot 1.5\text{H}_2\text{O}$ were harvested from the reaction tube following slow evaporation of solvent.

S3. Refinement

All H-atoms on the water molecules were located in a difference map and restrained with O—H distances of 0.85 Å, H···H separations of 1.39 Å, and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$.

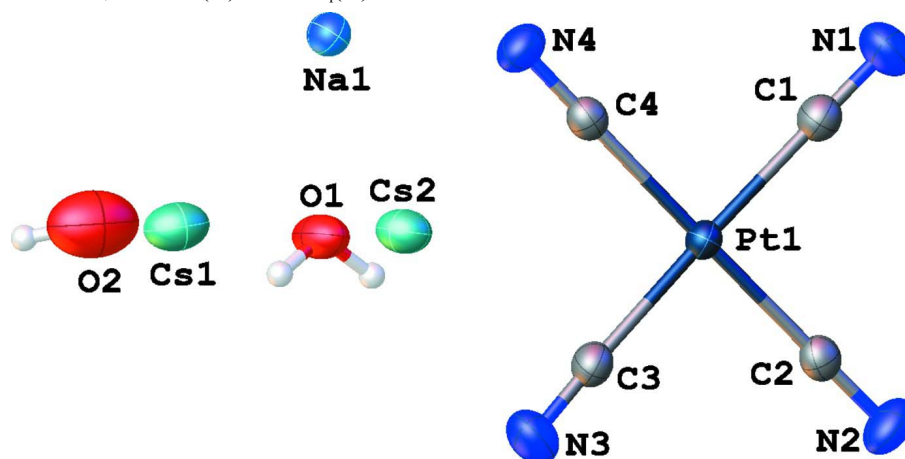


Figure 1

The asymmetric unit of $\text{Cs}_{1.5}\text{Na}_{0.5}\text{Pt}(\text{CN})_4 \cdot 1.5\text{H}_2\text{O}$ with the atom-numbering scheme. Displacement ellipsoids for non-hydrogen atoms are drawn at the 50% probability level.

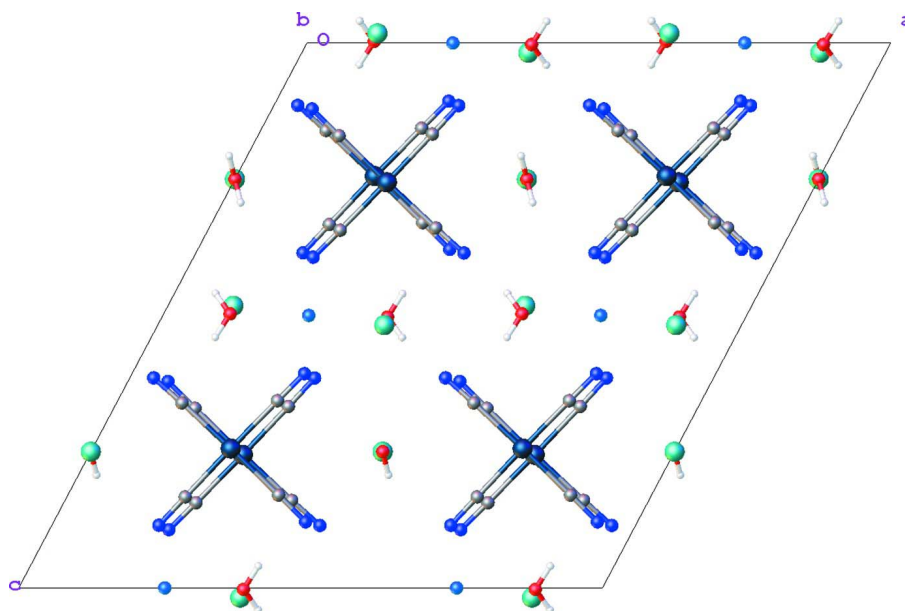


Figure 2

A packing diagram for $\text{Cs}_{1.5}\text{Na}_{0.5}\text{Pt}(\text{CN})_4 \cdot 1.5\text{H}_2\text{O}$ along the b axis illustrating the tetracyanidoplatinate stacking.

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Crystal data

Cs_{1.5}Na_{0.5}[Pt(CN)₄]·1.5H₂O $M_r = 1074.11$ Monoclinic, $C2/c$ Hall symbol: $-C\ 2yc$ $a = 17.4090\ (5)\ \text{\AA}$ $b = 7.2190\ (1)\ \text{\AA}$ $c = 18.3921\ (5)\ \text{\AA}$ $\beta = 117.858\ (4)^\circ$ $V = 2043.56\ (11)\ \text{\AA}^3$ $Z = 4$ $F(000) = 1864$ $D_x = 3.491\ \text{Mg m}^{-3}$ Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 6424 reflections

 $\theta = 3.1\text{--}25.6^\circ$ $\mu = 18.99\ \text{mm}^{-1}$ $T = 290\ \text{K}$

Prism, colorless

 $0.20 \times 0.14 \times 0.08\ \text{mm}$

Data collection

Oxford Diffraction Excalibur-E

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 16.0514 pixels mm^{-1} ω scans

Absorption correction: multi-scan

(CrysAlis PRO; Oxford Diffraction, 2010)

 $T_{\min} = 0.471$, $T_{\max} = 1.00$

8164 measured reflections

1949 independent reflections

1789 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.019$ $\theta_{\max} = 25.7^\circ$, $\theta_{\min} = 3.1^\circ$ $h = -21 \rightarrow 21$ $k = -8 \rightarrow 8$ $l = -22 \rightarrow 22$

Refinement

Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.014$ $wR(F^2) = 0.034$ $S = 1.15$

1949 reflections

126 parameters

6 restraints

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier

map

Hydrogen site location: difference Fourier map

H atoms treated by a mixture of independent and constrained refinement

 $w = 1/[\sigma^2(F_o^2) + (0.0147P)^2 + 4.0939P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} = 0.002$ $\Delta\rho_{\max} = 0.63\ \text{e \AA}^{-3}$ $\Delta\rho_{\min} = -0.47\ \text{e \AA}^{-3}$ Extinction correction: SHELXL97 (Sheldrick, 2008), $F_c^* = kF_c[1 + 0.001xF_c^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.000819 (19)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cs1	0.0000	1.18745 (7)	-0.2500	0.04903 (13)
Cs2	0.111975 (18)	0.76781 (4)	-0.017780 (19)	0.03819 (9)

Na1	0.2500	0.2500	0.0000	0.0307 (5)
Pt1	0.236863 (10)	0.51660 (2)	0.244311 (9)	0.02326 (7)
C1	0.3610 (3)	0.5200 (6)	0.3297 (3)	0.0321 (10)
C2	0.2026 (3)	0.5153 (5)	0.3330 (2)	0.0285 (9)
C3	0.1120 (3)	0.5245 (6)	0.1605 (3)	0.0298 (9)
C4	0.2736 (3)	0.5128 (5)	0.1564 (2)	0.0267 (9)
N1	0.4315 (3)	0.5232 (6)	0.3789 (3)	0.0477 (11)
N2	0.1834 (3)	0.5155 (6)	0.3851 (3)	0.0446 (10)
N3	0.0407 (3)	0.5366 (6)	0.1146 (3)	0.0465 (10)
N4	0.2955 (3)	0.5061 (5)	0.1069 (2)	0.0376 (9)
O1	0.1138 (2)	0.2401 (5)	-0.0028 (2)	0.0443 (9)
H1A	0.109 (3)	0.213 (8)	0.040 (2)	0.066*
H1B	0.070 (2)	0.289 (7)	-0.040 (2)	0.066*
O2	0.0000	0.7576 (8)	-0.2500	0.087 (2)
H2	-0.031 (5)	0.698 (5)	-0.2927 (19)	0.131*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cs1	0.0443 (2)	0.0501 (3)	0.0628 (3)	0.000	0.0335 (2)	0.000
Cs2	0.02998 (15)	0.04395 (17)	0.04217 (17)	0.00112 (12)	0.01814 (13)	0.00518 (13)
Na1	0.0286 (12)	0.0374 (13)	0.0269 (12)	-0.0005 (10)	0.0135 (10)	0.0005 (10)
Pt1	0.02326 (9)	0.02732 (10)	0.01992 (9)	-0.00030 (6)	0.01069 (7)	-0.00112 (6)
C1	0.033 (2)	0.035 (2)	0.029 (2)	-0.0009 (19)	0.016 (2)	-0.0013 (19)
C2	0.028 (2)	0.028 (2)	0.027 (2)	-0.0014 (17)	0.0107 (18)	-0.0025 (17)
C3	0.032 (2)	0.034 (2)	0.026 (2)	-0.0021 (18)	0.0149 (19)	-0.0017 (18)
C4	0.025 (2)	0.026 (2)	0.026 (2)	0.0001 (17)	0.0094 (17)	-0.0009 (17)
N1	0.031 (2)	0.059 (3)	0.043 (2)	-0.0010 (19)	0.0084 (19)	-0.003 (2)
N2	0.059 (3)	0.050 (2)	0.038 (2)	-0.004 (2)	0.033 (2)	-0.0024 (19)
N3	0.032 (2)	0.056 (3)	0.042 (2)	-0.0005 (19)	0.0088 (19)	-0.004 (2)
N4	0.043 (2)	0.044 (2)	0.034 (2)	-0.0008 (18)	0.0247 (18)	-0.0023 (17)
O1	0.0303 (16)	0.066 (2)	0.038 (2)	0.0061 (16)	0.0175 (15)	0.0116 (17)
O2	0.083 (5)	0.069 (4)	0.127 (7)	0.000	0.063 (5)	0.000

Geometric parameters (Å, °)

Cs1—O2	3.103 (6)	Pt1—C2	1.982 (4)
Cs1—N1 ⁱ	3.464 (4)	Pt1—C1	1.991 (4)
Cs2—N1 ⁱⁱ	3.191 (4)	Pt1—C3	1.993 (4)
Cs2—N4 ⁱ	3.227 (4)	Pt1—C4	1.996 (4)
Cs2—N3 ⁱⁱⁱ	3.262 (4)	C1—N1	1.135 (6)
Cs2—N2 ^{iv}	3.316 (4)	C2—N2	1.153 (6)
Cs2—O1 ^v	3.420 (4)	C3—N3	1.132 (6)
Cs2—N4	3.491 (4)	C4—N4	1.141 (5)
Na1—O1	2.349 (3)	O1—H1A	0.85 (4)
Na1—N2 ^{vi}	2.527 (4)	O1—H1B	0.83 (4)
Na1—N4	2.541 (4)	O2—H2	0.84 (3)

O2—Cs1—N1 ⁱ	63.96 (7)	C4—Cs2—N2 ^{ix}	63.43 (9)
O2—Cs1—N1 ⁱⁱ	63.96 (7)	N1 ⁱⁱ —Cs2—C3	110.04 (10)
N1 ⁱ —Cs1—N1 ⁱⁱ	127.93 (15)	N4 ⁱ —Cs2—C3	153.14 (10)
O2—Cs1—N3 ^{vii}	124.57 (7)	N3 ⁱⁱⁱ —Cs2—C3	80.06 (10)
N1 ⁱ —Cs1—N3 ^{vii}	169.41 (10)	N2 ^{iv} —Cs2—C3	109.76 (10)
N1 ⁱⁱ —Cs1—N3 ^{vii}	61.00 (10)	O1 ^v —Cs2—C3	113.80 (9)
O2—Cs1—N3 ^{viii}	124.57 (7)	N4—Cs2—C3	62.76 (9)
N1 ⁱ —Cs1—N3 ^{viii}	61.00 (10)	N1 ^{ix} —Cs2—C3	61.13 (9)
N1 ⁱⁱ —Cs1—N3 ^{viii}	169.41 (10)	N3—Cs2—C3	17.67 (9)
N3 ^{vii} —Cs1—N3 ^{viii}	110.86 (14)	C4—Cs2—C3	45.64 (9)
O2—Cs1—N4 ⁱⁱ	67.01 (6)	N2 ^{ix} —Cs2—C3	92.48 (9)
N1 ⁱ —Cs1—N4 ⁱⁱ	82.40 (9)	N1 ⁱⁱ —Cs2—C1 ^{ix}	89.08 (11)
N1 ⁱⁱ —Cs1—N4 ⁱⁱ	77.84 (9)	N4 ⁱ —Cs2—C1 ^{ix}	110.29 (9)
N3 ^{vii} —Cs1—N4 ⁱⁱ	106.38 (9)	N3 ⁱⁱⁱ —Cs2—C1 ^{ix}	123.44 (10)
N3 ^{viii} —Cs1—N4 ⁱⁱ	99.28 (9)	N2 ^{iv} —Cs2—C1 ^{ix}	151.87 (10)
O2—Cs1—N4 ⁱ	67.01 (6)	O1 ^v —Cs2—C1 ^{ix}	56.47 (9)
N1 ⁱ —Cs1—N4 ⁱ	77.84 (9)	N4—Cs2—C1 ^{ix}	88.55 (9)
N1 ⁱⁱ —Cs1—N4 ⁱ	82.40 (9)	N1 ^{ix} —Cs2—C1 ^{ix}	17.65 (9)
N3 ^{vii} —Cs1—N4 ⁱ	99.28 (9)	N3—Cs2—C1 ^{ix}	62.37 (9)
N3 ^{viii} —Cs1—N4 ⁱ	106.38 (9)	C4—Cs2—C1 ^{ix}	73.70 (9)
N4 ⁱⁱ —Cs1—N4 ⁱ	134.02 (12)	N2 ^{ix} —Cs2—C1 ^{ix}	59.27 (9)
O2—Cs1—N2 ^{viii}	125.63 (6)	C3—Cs2—C1 ^{ix}	57.73 (9)
N1 ⁱ —Cs1—N2 ^{viii}	104.50 (9)	O1—Na1—O1 ^x	180.00 (17)
N1 ⁱⁱ —Cs1—N2 ^{viii}	105.13 (9)	O1—Na1—N2 ^{vi}	93.58 (13)
N3 ^{vii} —Cs1—N2 ^{viii}	65.76 (9)	O1 ^x —Na1—N2 ^{vi}	86.42 (13)
N3 ^{viii} —Cs1—N2 ^{viii}	75.49 (9)	O1—Na1—N2 ^{iv}	86.42 (13)
N4 ⁱⁱ —Cs1—N2 ^{viii}	167.20 (9)	O1 ^x —Na1—N2 ^{iv}	93.58 (13)
N4 ⁱ —Cs1—N2 ^{viii}	58.66 (9)	N2 ^{vi} —Na1—N2 ^{iv}	180.00 (16)
O2—Cs1—N2 ^{vii}	125.63 (6)	O1—Na1—N4 ^x	90.84 (13)
N1 ⁱ —Cs1—N2 ^{vii}	105.13 (9)	O1 ^x —Na1—N4 ^x	89.16 (13)
N1 ⁱⁱ —Cs1—N2 ^{vii}	104.50 (9)	N2 ^{vi} —Na1—N4 ^x	90.85 (13)
N3 ^{vii} —Cs1—N2 ^{vii}	75.49 (9)	N2 ^{iv} —Na1—N4 ^x	89.15 (13)
N3 ^{viii} —Cs1—N2 ^{vii}	65.76 (9)	O1—Na1—N4	89.16 (13)
N4 ⁱⁱ —Cs1—N2 ^{vii}	58.66 (9)	O1 ^x —Na1—N4	90.84 (13)
N4 ⁱ —Cs1—N2 ^{vii}	167.20 (9)	N2 ^{vi} —Na1—N4	89.15 (13)
N2 ^{viii} —Cs1—N2 ^{vii}	108.74 (13)	N2 ^{iv} —Na1—N4	90.85 (13)
O2—Cs1—C1 ⁱⁱ	66.00 (7)	N4 ^x —Na1—N4	180.00 (18)
N1 ⁱ —Cs1—C1 ⁱⁱ	126.47 (9)	C2—Pt1—C1	89.08 (17)
N1 ⁱⁱ —Cs1—C1 ⁱⁱ	17.94 (9)	C2—Pt1—C3	89.86 (17)
N3 ^{vii} —Cs1—C1 ⁱⁱ	63.92 (10)	C1—Pt1—C3	177.41 (17)
N3 ^{viii} —Cs1—C1 ⁱⁱ	154.32 (10)	C2—Pt1—C4	178.54 (16)
N4 ⁱⁱ —Cs1—C1 ⁱⁱ	61.35 (9)	C1—Pt1—C4	89.91 (17)
N4 ⁱ —Cs1—C1 ⁱⁱ	99.31 (9)	C3—Pt1—C4	91.18 (16)
N2 ^{viii} —Cs1—C1 ⁱⁱ	119.49 (9)	N1—C1—Pt1	179.2 (4)
N2 ^{vii} —Cs1—C1 ⁱⁱ	88.95 (9)	N1—C1—Cs1 ⁱ	70.0 (3)
O2—Cs1—C1 ⁱ	66.00 (7)	Pt1—C1—Cs1 ⁱ	110.74 (16)
N1 ⁱ —Cs1—C1 ⁱ	17.94 (9)	N1—C1—Cs2 ^{vi}	69.5 (3)
N1 ⁱⁱ —Cs1—C1 ⁱ	126.47 (9)	Pt1—C1—Cs2 ^{vi}	110.15 (16)

N3 ^{vii} —Cs1—C1 ⁱ	154.32 (10)	Cs1 ⁱ —C1—Cs2 ^{vi}	110.37 (11)
N3 ^{viii} —Cs1—C1 ⁱ	63.92 (10)	N2—C2—Pt1	179.4 (4)
N4 ⁱⁱ —Cs1—C1 ⁱ	99.31 (9)	N2—C2—Cs1 ^{vii}	75.9 (3)
N4 ⁱ —Cs1—C1 ⁱ	61.35 (9)	Pt1—C2—Cs1 ^{vii}	104.31 (14)
N2 ^{viii} —Cs1—C1 ⁱ	88.95 (9)	N2—C2—Cs2 ^{vi}	73.6 (3)
N2 ^{vii} —Cs1—C1 ⁱ	119.49 (9)	Pt1—C2—Cs2 ^{vi}	106.10 (15)
C1 ⁱⁱ —Cs1—C1 ⁱ	132.01 (13)	Cs1 ^{vii} —C2—Cs2 ^{vi}	148.78 (12)
O2—Cs1—C3 ^{viii}	123.99 (6)	N3—C3—Pt1	176.8 (4)
N1 ⁱ —Cs1—C3 ^{viii}	61.52 (10)	N3—C3—Cs1 ^{vii}	70.7 (3)
N1 ⁱⁱ —Cs1—C3 ^{viii}	165.39 (9)	Pt1—C3—Cs1 ^{vii}	106.37 (15)
N3 ^{vii} —Cs1—C3 ^{viii}	108.55 (9)	N3—C3—Cs2	75.9 (3)
N3 ^{viii} —Cs1—C3 ^{viii}	17.71 (9)	Pt1—C3—Cs2	104.23 (15)
N4 ⁱⁱ —Cs1—C3 ^{viii}	116.12 (9)	Cs1 ^{vii} —C3—Cs2	110.00 (11)
N4 ⁱ —Cs1—C3 ^{viii}	89.80 (9)	N4—C4—Pt1	178.2 (4)
N2 ^{viii} —Cs1—C3 ^{viii}	60.29 (9)	N4—C4—Cs2	74.1 (3)
N2 ^{vii} —Cs1—C3 ^{viii}	81.03 (9)	Pt1—C4—Cs2	107.38 (14)
C1 ⁱⁱ —Cs1—C3 ^{viii}	168.91 (9)	N4—C4—Cs1 ⁱ	71.4 (3)
C1 ⁱ —Cs1—C3 ^{viii}	58.23 (9)	Pt1—C4—Cs1 ⁱ	107.30 (14)
N1 ⁱⁱ —Cs2—N4 ⁱ	92.57 (11)	Cs2—C4—Cs1 ⁱ	144.19 (12)
N1 ⁱⁱ —Cs2—N3 ⁱⁱⁱ	70.67 (10)	C1—N1—Cs2 ^{xi}	151.8 (4)
N4 ⁱ —Cs2—N3 ⁱⁱⁱ	122.44 (10)	C1—N1—Cs1 ⁱ	92.0 (3)
N1 ⁱⁱ —Cs2—N2 ^{iv}	118.92 (11)	Cs2 ^{xi} —N1—Cs1 ⁱ	93.27 (11)
N4 ⁱ —Cs2—N2 ^{iv}	68.68 (9)	C1—N1—Cs2 ^{vi}	92.8 (3)
N3 ⁱⁱⁱ —Cs2—N2 ^{iv}	72.87 (11)	Cs2 ^{xi} —N1—Cs2 ^{vi}	107.60 (12)
N1 ⁱⁱ —Cs2—O1 ^v	62.99 (9)	Cs1 ⁱ —N1—Cs2 ^{vi}	121.89 (13)
N4 ⁱ —Cs2—O1 ^v	63.17 (8)	C2—N2—Na1 ^{ix}	119.8 (3)
N3 ⁱⁱⁱ —Cs2—O1 ^v	133.63 (9)	C2—N2—Cs2 ^{xii}	140.8 (3)
N2 ^{iv} —Cs2—O1 ^v	131.82 (9)	Na1 ^{ix} —N2—Cs2 ^{xii}	95.96 (12)
N1 ⁱⁱ —Cs2—N4	172.46 (10)	C2—N2—Cs1 ^{vii}	86.4 (3)
N4 ⁱ —Cs2—N4	94.96 (9)	Na1 ^{ix} —N2—Cs1 ^{vii}	95.09 (12)
N3 ⁱⁱⁱ —Cs2—N4	104.84 (9)	Cs2 ^{xii} —N2—Cs1 ^{vii}	107.33 (11)
N2 ^{iv} —Cs2—N4	64.01 (10)	C2—N2—Cs2 ^{vi}	89.0 (3)
O1 ^v —Cs2—N4	121.04 (8)	Na1 ^{ix} —N2—Cs2 ^{vi}	81.26 (11)
N1 ⁱⁱ —Cs2—N1 ^{ix}	72.40 (12)	Cs2 ^{xii} —N2—Cs2 ^{vi}	80.48 (9)
N4 ⁱ —Cs2—N1 ^{ix}	115.65 (10)	Cs1 ^{vii} —N2—Cs2 ^{vi}	171.76 (12)
N3 ⁱⁱⁱ —Cs2—N1 ^{ix}	110.69 (10)	C3—N3—Cs2 ⁱⁱⁱ	133.2 (3)
N2 ^{iv} —Cs2—N1 ^{ix}	168.32 (10)	C3—N3—Cs1 ^{vii}	91.6 (3)
O1 ^v —Cs2—N1 ^{ix}	54.15 (9)	Cs2 ⁱⁱⁱ —N3—Cs1 ^{vii}	112.71 (12)
N4—Cs2—N1 ^{ix}	104.40 (9)	C3—N3—Cs2	86.4 (3)
N1 ⁱⁱ —Cs2—N3	93.85 (10)	Cs2 ⁱⁱⁱ —N3—Cs2	113.08 (12)
N4 ⁱ —Cs2—N3	170.13 (9)	Cs1 ^{vii} —N3—Cs2	117.54 (12)
N3 ⁱⁱⁱ —Cs2—N3	66.92 (12)	C4—N4—Na1	123.3 (3)
N2 ^{iv} —Cs2—N3	114.26 (10)	C4—N4—Cs2 ⁱ	144.7 (3)
O1 ^v —Cs2—N3	113.53 (9)	Na1—N4—Cs2 ⁱ	91.37 (11)
N4—Cs2—N3	78.72 (9)	C4—N4—Cs2	87.6 (3)
N1 ^{ix} —Cs2—N3	59.58 (10)	Na1—N4—Cs2	91.55 (11)
N1 ⁱⁱ —Cs2—C4	155.22 (10)	Cs2 ⁱ —N4—Cs2	85.04 (9)
N4 ⁱ —Cs2—C4	109.89 (10)	C4—N4—Cs1 ⁱ	91.0 (3)

N3 ⁱⁱⁱ —Cs2—C4	103.78 (10)	Na1—N4—Cs1 ⁱ	97.36 (11)
N2 ^{iv} —Cs2—C4	80.30 (10)	Cs2 ⁱ —N4—Cs1 ⁱ	90.55 (9)
O1 ^v —Cs2—C4	117.45 (8)	Cs2—N4—Cs1 ⁱ	170.16 (12)
N4—Cs2—C4	18.33 (9)	Na1—O1—Cs2 ^{xiii}	90.18 (10)
N1 ^{ix} —Cs2—C4	88.03 (9)	Na1—O1—H1A	121 (4)
N3—Cs2—C4	62.56 (9)	Cs2 ^{xiii} —O1—H1A	81 (4)
N1 ⁱⁱ —Cs2—N2 ^{ix}	122.71 (10)	Na1—O1—H1B	122 (4)
N4 ⁱ —Cs2—N2 ^{ix}	62.33 (9)	Cs2 ^{xiii} —O1—H1B	113 (4)
N3 ⁱⁱⁱ —Cs2—N2 ^{ix}	166.50 (10)	H1A—O1—H1B	115 (4)
N2 ^{iv} —Cs2—N2 ^{ix}	99.52 (9)	Cs1—O2—Cs2 ^{xiv}	88.88 (9)
O1 ^v —Cs2—N2 ^{ix}	59.73 (8)	Cs1—O2—Cs2	88.88 (9)
N4—Cs2—N2 ^{ix}	61.66 (9)	Cs2 ^{xiv} —O2—Cs2	177.76 (18)
N1 ^{ix} —Cs2—N2 ^{ix}	74.63 (9)	Cs1—O2—H2	121 (3)
N3—Cs2—N2 ^{ix}	107.83 (9)	Cs2—O2—H2	147 (4)

Symmetry codes: (i) $-x+1/2, -y+3/2, -z$; (ii) $x-1/2, -y+3/2, z-1/2$; (iii) $-x, -y+1, -z$; (iv) $x, -y+1, z-1/2$; (v) $x, y+1, z$; (vi) $-x+1/2, y-1/2, -z+1/2$; (vii) $-x, -y+2, -z$; (viii) $x, -y+2, z-1/2$; (ix) $-x+1/2, y+1/2, -z+1/2$; (x) $-x+1/2, -y+1/2, -z$; (xi) $x+1/2, -y+3/2, z+1/2$; (xii) $x, -y+1, z+1/2$; (xiii) $x, y-1, z$; (xiv) $-x, y, -z-1/2$.

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1A \cdots N1 ^{vi}	0.85 (2)	2.37 (3)	3.154 (6)	155 (5)
O1—H1B \cdots N3 ⁱⁱⁱ	0.83 (2)	2.17 (2)	2.982 (5)	166 (5)

Symmetry codes: (iii) $-x, -y+1, -z$; (vi) $-x+1/2, y-1/2, -z+1/2$.