Alkali Metal Complexes of Aromatic Polycarboxylates—a Balance of π-Stacking and Coordinate Bonding Interactions?

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Alkali Metal Complexes of Aromatic Polycarboxylates—a Balance of π-Stacking and Coordinate Bonding Interactions?

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Crystal structure determinations of, in most cases, hydrated, alkali metal derivatives of the dicarboxylic acids, 2,2′-bipyridine-3,3′-dicarboxylic acid (H$_2$BDC) and chelidamic acid (4-hydroxypyridine-2,6-dicarboxylic acid, H$_2$CHEL) show numerous similarities, such as in the predominance of *O*-coordination in generating solid state polymers in which parallel arrays of the essentially planar ligand ring units are apparent, though not necessarily indicative of conventional π-stacking interactions, and some unanticipated differences. In particular, all species derived from chelidamic acid, including its diammonium compound, appear to be complexes of the partially deprotonated pyridone form of this ligand. In both systems, close contacts between atoms constituting the aromatic entities take a variety of forms depending upon the associated metal.

Keywords: Aromatic ligand interactions; Alkali metal complexes; Crystal structures

INTRODUCTION

The challenging problem of controlling the structure of solids [1] demands an improved understanding of the multitude of forces which may be considered to act in condensed phases and which are important in all supramolecular chemistry [2]. An interaction commonly encountered in systems which range from those of apolar neutral molecules [3,4] to those of highly polar metal complexes [5,6], is that arising from the presence of aromatic moieties. Conventionally, this is considered to be an interaction which may take several forms, as defined in the expressions "π-stacking", "edge-to-face" and "vertex-to-face" attractions [1–12]. In the presence of both organic and metallic cations, "cation–π" interactions may also be important [13–17]. Evidence for the structural influences of all these factors can be found in X-ray crystallographic investigations of many formally "simple" metal derivatives of functionalised aromatic systems [5,18–20], and their deliberate exploitation has been involved in the "crystal engineering" of transition metal complexes [21–25], though it is perhaps reasonable to anticipate that weak coordinate bonding in alkali metal ion complexes may allow such intermolecular forces to exert their influence most strongly. In a continuing exploration of this hypothesis, we have conducted crystallographic studies of the alkali metal ion complexes of two aza-aromatic dicarboxylate systems, chelidamic acid (4-hydroxypyridine-2,6-dicarboxylic acid, H$_2$CHEL) and 2,2′-bipyridine-3,3′-dicarboxylic acid (H$_2$BDC), both formally sources of carboxylate dianions. In the solid state, the proton coordination chemistry has been established for chelidamate dianion, where a structure determination of the acid as its monohydrate [26] shows H$^+$ to be formally bound to one carboxylate and to the pyridine nitrogen (as well as to the 4-oxygen, though this is a complicated issue explored further in the present work), rather than to two carboxylates, with the structure clearly reflecting the importance of both proton coordination (H-bonding) and π-stacking interactions. Significantly, there is a definite association of a proton with the 4-oxo substituent, indicating that crystalline chelidamic

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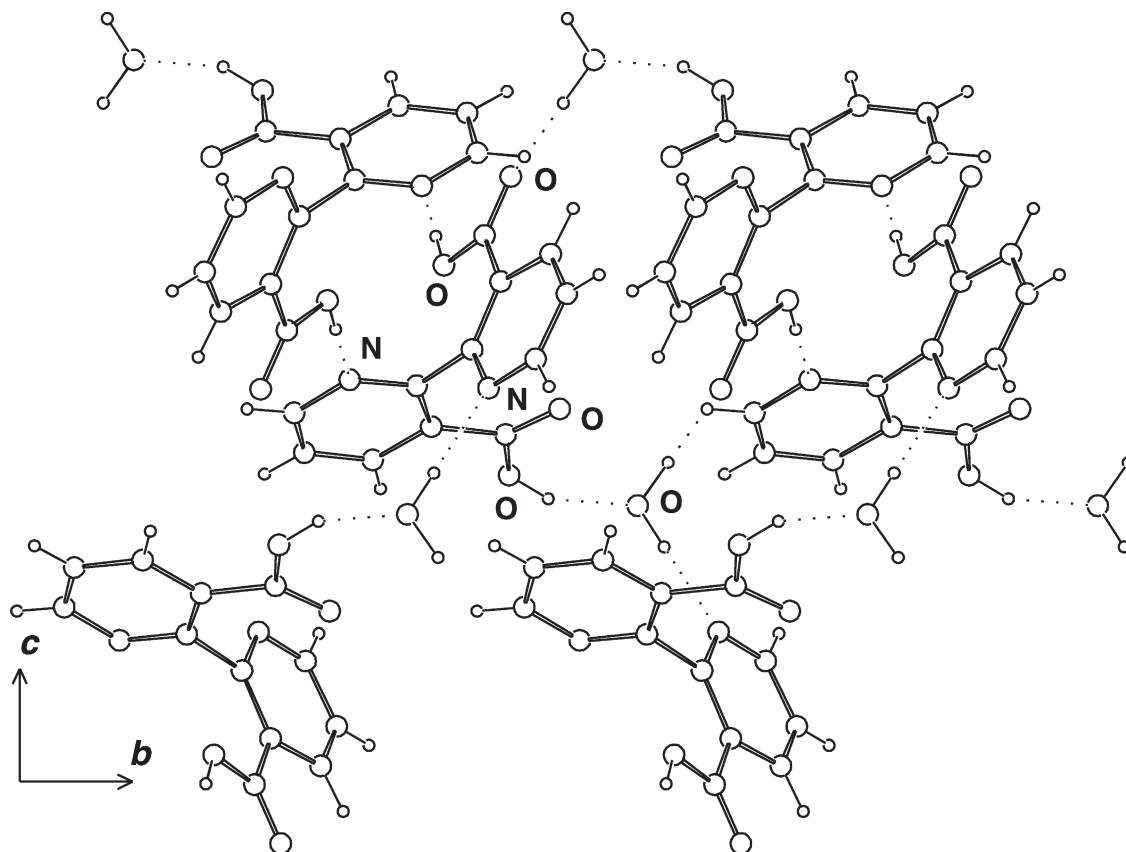*Corresponding author. E-mail: gak@chem.uwa.edu.au

FIGURE 1   Portion of the unit cell contents of H$_2$BDC, down *a*, showing the proton coordination network (after Ref. [27]).

acid should be regarded as a 4-hydroxypyridine, rather than a pyrid-4-one derivative. 2,2′-bipyridine-3,3′-dicarboxylic acid also crystallises as a monohydrate [27] but in this case, like dipicolinic acid [28] (a close analogue of chelidamic acid), both protons appear to associate most strongly with the carboxylate sites. The structure, Fig. 1, nonetheless, has some interesting features, including a *cisoid*, chiral twisting (necessarily homo- throughout the space group $P2_12_12_1$) of the biaryl unit (C$_5$N/C$_5$N interplanar dihedral angle 79.5(2)°, N—C—C—N torsion 77.0(7)°) which allows carbonyl oxygen atoms to approach (at ∼2.8 Å distance) the C2 (2′) atoms of the linked ring; H-bonding of one of the carboxyl group protons to one nitrogen of another diacid molecule results in helices about the 2_1 screw axes parallel to *a*. H-bonding of the other carboxylic group proton is to the water molecule, the hydrogens of which interact with the other nitrogen and an unprotonated carboxylate oxygen, linking successive helices (Fig. 1). Parallel arrays of the pyridine rings are also apparent but ring carbon/ring carbon contacts are distant except for separations as short as 3.348(2) Å (C4···C5′) in nonparallel rings where interactions involving carboxyl group atoms and ring carbon atoms may

be comparable. This evidence of numerous factors at work in the structure of the proton complex foreshadows rather complicated possible consequences of the introduction of metal ions, as indeed may be true of the known instances of structures involving transition metals [27,29–36].

EXPERIMENTAL

Synthesis

Commerical chelidamic acid (Aldrich) was used as received, while 2,2′-bipyridine-3,3′-dicarboxylic acid was prepared as described in the literature [37]. Aiming at the preparation of M$_2$L species, alkali metal derivatives were prepared by mixing equimolar amounts of the acid and alkali metal carbonate in a small volume of water (∼10 mL/g of diacid), heating the mixture until carbon dioxide evolution had ceased and then evaporating the resultant solution to dryness. The crude white powders obtained were then used in crystallisation experiments. The ammonium derivative of chelidamic acid was obtained by dissolving the acid in excess concentrated aqueous ammonia and allowing this solution to evaporate to dryness.

Crystallisation

Alkali Metal Derivatives of 2,2′-Bipyridine-3,3′-dicarboxylic Acid

For Na, K, Rb and Cs, material adequate for the structural work resulted on allowing aqueous solutions of the crude solids to slowly evaporate at ambient temperature. This procedure was unsatisfactory for the Li compound, which appeared to be extremely soluble in water, although, after experiments with numerous solvents, it was found that by adding dimethyl sulfoxide to the aqueous solution and then heating the mixture at ~40°C to slowly evaporate out the water, colourless aggregates could be obtained.

Alkali Metal Derivatives of Chelidamic Acid

Slow evaporation of aqueous solutions of the various chelidamates provided seemingly crystalline precipitates which rapidly effloresced to give powders, except in the case of the potassium compound. Vapour diffusion of ethanol into aqueous solutions of the sodium, ammonium and potassium compounds provided larger, needle-like crystals, all of sufficient stability to be transferred to a capillary or the diffractometer without noticeable deterioration, though the stoichiometry of the sodium compound was not that anticipated (see below). Vapour diffusion of ethanol into aqueous solutions of the Rb and Cs compounds provided crystals but always as clusters of extremely fine, very long needles, and only after numerous attempts was a sample of the caesium compound obtained from which a useful crystal could be obtained. Vapour diffusion of acetonitrile into an aqueous solution of the Li compound resulted in the deposition of an oil which, after substitution of acetonitrile by ethanol as the diffusing solvent, underwent a slow (several weeks) transformation into a mixture of colourless crystals and amorphous white powder. A specimen was selected from this mixture for the structure determination.

Structure Determinations

Full spheres of low-temperature ($T \sim 153$ K) CCD area detector diffractometer data were measured (Bruker AXS instrument; ω-scans; monochromatic Mo-K_α radiation $\lambda = 0.7107_3$ Å) yielding $N_{t(otal)}$ reflections, merging to N unique after 'empirical'/multiscan absorption correction (proprietary software; R_{int} quoted), N_o with $F > 4\sigma(F)$ considered 'observed' and used in the full-matrix least squares refinements, refining anisotropic thermal parameter forms for the non-hydrogen atoms and $(x, y, z, U_{iso})_H$. (Individual variations in procedure, etc. are noted as "*Variata*".) Conventional residuals R, R_w on $|F|$ (weights: $(\sigma^2(F) + 0.0004F^2)^{-1}$) are quoted at convergence. Neutral atom complex scattering factors were employed within the XTAL 3.6 program system [38]. Pertinent results are given below and in the Tables and Figures, the latter showing 50% probability amplitude displacement envelopes for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å. Full .cif files (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre, #186683–186689; 190697–190699; 200924.

Disodium 2,2′-Bipyridine-3,3′-dicarboxylate Tetrahydrate

$C_{12}H_{14}N_2Na_2O_8$, $M = 360.23$, orthorhombic, space group $Pbcn$ (D_{2h}^{14}, No. 60), $a = 11.0514(6)$, $b = 6.5630(4)$, $c = 19.1323(1)$ Å, $V = 1388$ Å^3, D_c ($Z = 4$) $= 1.72_4$ g cm^{-3}. $\mu_{Mo} = 2.0$ cm^{-1}, specimen: $0.40 \times 0.25 \times 0.15$ mm, 'T'$_{min,max} = 0.74$, 0.86. $2\theta_{max} = 75°$, $N_t = 28326$, $N = 3651$ ($R_{int} = 0.034$), $N_o = 2811$, $R = 0.034$, $R_w = 0.042$, $|\Delta\rho_{max}| = 0.67(4)$ e Å^{-3}.

Dipotassium 2,2′-Bipyridine-3,3′-dicarboxylate Tetrahydrate, $C_{12}H_{14}K_2N_2O_8$,

$M = 392.45$, orthorhombic, space group $Pbcn$, $a = 11.677(5)$, $b = 6.967(4)$, $c = 19.414(9)$ Å, $V = 1579$ Å^3, $D_c = 1.65_0$ g cm^{-3}, $\mu_{Mo} = 6.4$ cm^{-1}, specimen: $0.60 \times 0.80 \times 0.90$ mm, 'T'$_{min,max} = 0.66$, 0.72. $2\theta_{max} = 65°$, N_t (hemisphere) $= 4549$, $N = 2861$ ($R_{int} = 0.057$), $N_o = 2154$, $R = 0.046$, $R_w = 0.066$, $|\Delta\rho_{max}| = 0.48(5)$ e Å^{-3}.

Variata: A hemisphere of data was measured at *ca.* 295 K using a single counter ("four circle") instrument and gaussian absorption correction. The results are presented in the same cell and coordinate settings as those for the Na analogue, which is isomorphous. The 'observed' criterion was $I > 3\sigma(I)$.

Dirubidium 2,2′-Bipyridine-3,3′-dicarboxylate Monohydrate

$C_{12}H_8N_2O_5Rb_2$, $M = 431.14$, orthorhombic, space group $Pnna$ (D_{2h}^6, No. 52), $a = 7.1943(6)$, $b = 16.5323(1)$, $c = 12.314(1)$ Å, $V = 1465$ Å^3, D_c ($Z = 4$) $= 1.95_5$ g cm^{-3}. $\mu_{Mo} = 67$ cm^{-1}, specimen: $0.35 \times 0.25 \times 0.10$ mm, 'T'$_{min,max} = 0.32$, 0.65. $2\theta_{max} = 75°$, $N_t = 28002$, $N = 3705$ ($R_{int} = 0.066$), $N_o = 2415$, $R = 0.027$, $R_w = 0.023$, $|\Delta\rho_{max}| = 1.3(4)$ e Å^{-3}.

Dicaesium 2,2′-Bipyridine-3,3′-dicarboxylate Monohydrate

$C_{12}H_8Cs_2N_2O_5$, $M = 526.02$, orthorhombic, space group $Pnna$, $a = 7.5957(3)$, $b = 17.1949(8)$, $c = 12.2581(6)$ Å, $V = 1601$ Å^3, $D_c = 2.18_2$ g cm^{-3}. $\mu_{Mo} = 48$ cm^{-1}, specimen: $0.24 \times 0.55 \times 0.11$ mm, 'T'$_{min,max}$

= 0.54, 0.80. $2\theta_{max} = 75°$, $N_t = 33147$, $N = 4215$ ($R_{int} = 0.035$), $N_o = 3112$, $R = 0.020$, $R_w = 0.020$, $|\Delta\rho_{max}| = 1.5(3)\,e\,\text{Å}^{-3}$. The structure was refined in the same cell and coordinate settings as those of the rubidium analogue, with which it is isomorphous.

Dilithium 4-Pyridone-2,6-dicarboxylate Trihydrate

$C_7H_9Li_2NO_8$, $M = 249.03$, monoclinic, space group $P2_1/n$ (C_{2h}^5, No. 14 (variant)), $a = 11.0594(7)$, $b = 7.1239(4)$, $c = 13.0607(8)\,\text{Å}$, $\beta = 90.659(1)°$, $V = 1029\,\text{Å}^3$, D_c ($Z = 4$) $= 1.60_7\,\text{g cm}^{-3}$. $\mu_{Mo} = 1.4\,\text{cm}^{-1}$, specimen: $0.18 \times 0.16 \times 0.12\,\text{mm}$, '$T$'$_{min,max} = 0.85$, 0.96. $2\theta_{max} = 75°$, $N_t = 20942$, $N = 5374$ ($R_{int} = 0.021$), $N_o = 4556$, $R = 0.032$, $R_w = 0.042$, $|\Delta\rho_{max}| = 0.64(2)\,e\,\text{Å}^{-3}$.

Deca-aquapentasodium (4-Pyridone-2,6-dicarboxylate)-tris(6-hydroxycarbonyl-4-pyridone-2-carboxylate) 18.6 Hydrate

$C_{28}H_{70.1}N_4Na_5O_{48.6}$, $M \sim 1357$, triclinic, space group $P\bar{1}$ (C_i^1, No. 2), $a = 7.1691(7)$, $b = 10.609(4)$, $c = 18.449(2)\,\text{Å}$, $\alpha = 104.160(2)$, $\beta = 93.086(2)$, $\gamma = 93.699(2)°$, $V = 1354\,\text{Å}^3$, D_c ($Z = 1$) $= 1.66_1\,\text{g cm}^{-3}$. $\mu_{Mo} = 1.9\,\text{cm}^{-1}$, specimen: $0.15 \times 0.07 \times 0.05\,\text{mm}$, '$T$'$_{min,max} = 0.73$, 0.91. $2\theta_{max} = 58°$, $N_t = 20786$, $N = 7125$ ($R_{int} = 0.029$), $N_o = 5130$, $R = 0.065$, $R_w = 0.081$, $|\Delta\rho_{max}| = 1.23(4)\,e\,\text{Å}^{-3}$.

Variata: Residues modelled as lattice water molecule oxygen atoms O(10)–O(14) were modelled as disordered over pairs of sites, occupancies $x = 0.794(5)$, $1 - x$. O(15) was modelled as disordered over a pair of sites of equal occupancy. O(16,17) site occupancies refined to 0.207(5) (N.B. $\approx 1 - 0.794(5)$) and 0.18(1). $(x, y, z, U_{iso})_H$ were refined for hydrogen atoms in association with the chelidamate and coordinated water moieties, including the two nitrogen atoms. The 0.5H aliquot required to balance the charge is crystallographically indeterminate.

Dipotassium 4-Pyridone-2,6-dicarboxylate 0.75 Hydrate ≡ Octapotassium Tetrakis(4-pyridone-2,6-dicarboxylate) Hexahydrate

$C_{28}H_{24}K_8N_4O_{26}$, $M = 1145.29$, triclinic, space group $P\bar{1}$, $a = 3.6826(3)$, $b = 19.596(2)$, $c = 29.829(3)\,\text{Å}$, $\alpha = 107.279(2)$, $\beta = 92.638(2)$, $\gamma = 94.464(2)°$, $V = 2044\,\text{Å}^3$, D_c ($Z = 2$) $= 1.86_1\,\text{g cm}^{-3}$. $\mu_{Mo} = 9.5\,\text{cm}^{-1}$, specimen: $0.70 \times 0.11 \times 0.10\,\text{mm}$, '$T$'$_{min,max} = 0.78$, 0.91. $2\theta_{max} = 58°$, $N_t = 42568$, $N = 10765$ ($R_{int} = 0.043$), $N_o = 8566$, $R = 0.064$, $R_w = 0.078$, $|\Delta\rho_{max}| = 1.54(5)\,e\,\text{Å}^{-3}$.

Variata: K(6) was modelled as disordered over two sites, occupancies $x = 0.865(4)$, $1 - x$, water molecule components associated with the minor

fragment not being located. Water molecule hydrogen atoms were not located.

Diammonium 4-Pyridone-2,6-dicarboxylate Monohydrate

$C_7H_{13}N_3O_6$, $M = 235.20$, monoclinic, space group $P2_1$ (C_2^2, No. 4), $a = 3.9334(9)$, $b = 16.702(4)$, $c = 8.015(2)\,\text{Å}$, $\beta = 103.017(6)°$, $V = 513.0\,\text{Å}^3$, D_c ($Z = 2$) $= 1.52_2\,\text{g cm}^{-3}$. $\mu_{Mo} = 1.3\,\text{cm}^{-1}$, specimen: $0.29 \times 0.13 \times 0.08\,\text{mm}$, '$T$'$_{min,max} = 0.70$, 0.96. $2\theta_{max} = 76°$, $N_t = 10553$, $N = 2770$ ($R_{int} = 0.037$), $N_o = 2460$, $R = 0.033$, $R_w = 0.038$, $|\Delta\rho_{max}| = 0.36(3)\,e\,\text{Å}^{-3}$.

Variata: The chirality of the structure was indeterminate and 'Friedel' data were merged in the final refinement cycles.

Tri-rubidium (4-Pyridone-2,6-dicarboxylate) (6-hydroxycarbonyl-4-pyridone-2-carboxylate) Hexahydrate

$C_{14}H_{21}N_2O_{16}Rb_3$, $M = 729.72$. Orthorhombic, space group $Pbca$ (D_{2h}^{15}, No. 61), $a = 7.044(3)$, $b = 31.980(8)$, $c = 20.517(13)\,\text{Å}$, $V = 4622\,\text{Å}^3$. D_c ($Z = 8$) $= 2.09_7\,\text{g cm}^{-3}$. $\mu_{Mo} = 64\,\text{cm}^{-1}$; specimen: $1.6 \times 0.03 \times 0.03\,\text{mm}$; '$T$'$_{min/max}$ 0.44. $2\theta_{max} = 50°$; $N_t = 36273$, $N = 4015$ ($R_{int} = 0.10$), $N_o = 2598$; $R = 0.061$, $R_w = 0.087$. $|\Delta\rho_{max}| = 1.6(2)\,e\,\text{Å}^{-3}$.

Variata. Weak and limited data would support meaningful anisotropic displacement parameter refinement for Rb only, C,N,O taking the isotropic form; ligand hydrogen atoms nevertheless were resolved in difference maps and included at estimated sites, those for the water molecules, less well secured, being omitted.

Dicaesium 4-Pyridone-2,6-dicarboxylate

$C_7H_3Cs_2NO_5$, $M = 446.91$, monoclinic, space group $P2_1/n$, $a = 3.9806(6)$, $b = 16.794(2)$, $c = 15.162(2)\,\text{Å}$, $\beta = 92.532(3)°$, $V = 1013\,\text{Å}^3$, D_c ($Z = 4$) $= 2.93_1\,\text{g cm}^{-3}$. $\mu_{Mo} = 72\,\text{cm}^{-1}$, specimen: $0.22 \times 0.06 \times 0.05\,\text{mm}$, '$T$'$_{min,max} = 0.47$, 0.89. $2\theta_{max} = 62.5°$, $N_t = 20672$, $N = 3293$ ($R_{int} = 0.068$), $N_o = 3062$, $R = 0.050$, $R_w = 0.085$, $|\Delta\rho_{max}| = 3.6(1)\,e\,\text{Å}^{-3}$.

Variata: Crystals formed as small, twinned laths; data were measured on the major reciprocal lattice component of a specimen obtained with one component predominant. Hydrogen atoms were included constrained at estimates in the refinement.

2,6-Diacetylpyridine

$C_9H_9NO_2$, $M = 163.20$, monoclinic, space group $P2_1/c$ (C_{2h}^5, No. 14), $a = 3.9445(8)$, $b = 8.2845(8)$, $c = 25.917(3)\,\text{Å}$, $\beta = 94.325(2)°$, $V = 844.5\,\text{Å}^3$, D_c ($Z = 4$) $= 1.28_3\,\text{g cm}^{-3}$. $\mu_{Mo} = 0.9\,\text{cm}^{-1}$, specimen: $0.38 \times 0.12 \times 0.10\,\text{mm}$, '$T$'$_{min,max} = 0.58$, 0.93, $2\theta_{max} =$

TABLE I   Metal environments, $M_2BDC\cdot 4H_2O$ (M = Na, K)

Atom	r	O(01)	O(02)	O(02^i)	O(31^{ii})	O(01^{iii})
O(31)	2.4362(8)	79.08(3)	90.03(3)	97.51(3)	100.23(3)	170.39(3)
	2.744(2)	*85.56(5)*	*90.87(5)*	*94.44(5)*	*100.39(5)*	*167.57(5)*
O(01)	2.4642(8)		165.98(3)	102.89(3)	66.08(2)	106.06(3)
	2.729(2)		*163.95(5)*	*102.04(6)*	*60.45(5)*	*106.19(6)*
O(02)	2.3741(8)			87.15(3)	107.84(3)	83.53(3)
	2.688(2)			*93.83(6)*	*105.05(6)*	*76.71(5)*
O(02^i)	2.4151(8)				156.63(3)	89.32(3)
	2.764(2)				*155.66(4)*	*87.15(6)*
O(31^{ii})	2.6260(8)					75.13(3)
	2.829(2)					*82.50(5)*
O(01^{ii})	2.4880(9)					
	2.809(2)					

Transformations of the asymmetric unit: i $1-x, 1-y, 1-z$ ii $3/2-x, y-1/2, z$ iii $1-x, y, 3/2-z$ iv $3/2-x, 1/2+y, z$
M—O(31)—M^{iv} 100.60(3), *94.92(5)*; C(31)—O(31)—M,M^{iv} 126.35(6), 130.99(6); *122.4(1), 137.2(1)*; M—O(01,02)—M^{iv} 103.79(3), 92.85(3); *95.71(6), 86.17(5)*°. H(01a)···O(32) (1/2 + x, 1(1/2) − y, 1 − z 2.06(2), *2.04(3)*; H(01b)···O(31) (1 (1/2) − x, y − 1/2, z) 1.98(2), *2.03(3)*; H(02a)···N (1 − x, y, 1 (1/2) − z) 2.01(2), *2.00(3)*; H(02b)···O(32) (x, y − 1, z) 1.96(2), *1.98(3)* Å.

Values for the *potassium* complex are given in *italics*. r Å is the metal–donor distance; other entries in the matrix are the angles (degrees) subtended by the atoms at the head of the relevant row and column.

58°, N_t = 17480, N = 2241 (R_{int} = 0.038), N_o = 1825, R = 0.040, R_w = 0.047, $|\Delta\rho_{max}|$ = 0.32(4) e Å^{-3}.

RESULTS AND DISCUSSION

Description of the Structures

Although chelidamic acid [26,39,40] is, in principle, a triprotic species, possibly existing in tautomeric (pyridone and hydroxypyridine) forms, there appears to be a large difference in basicity between the tri- and di-anionic forms, and the trianionic form detected in lanthanide ion complexes [41,42], has not been encountered in the present work. In the context of comparison with 2,2′-bipyridine-3,3′-dicarboxylic acid, in particular, we treat it as a dibasic acid, though proton distributions in its anions do prove to be somewhat complicated to describe, the structural results in fact supporting the proposal that the tautomeric form of a chelidamate species may be influenced by the associated cation [39,40].

Because of such complications, we commence our discussion with that of the ostensibly simpler systems involving the alkali metal ion derivatives of 2,2′-bipyridine-3,3′dicarboxylic acid, H_2BDC.

The results of low-temperature, single-crystal X-ray studies of alkali-metal ion derivatives of H_2BDC are consistent with their formulation, as given above and as intended by the method of synthesis chosen, as variously hydrated complexes of the doubly-deprotonated acid anion, BDC^{2-}, *i.e.* as $M_2BDC\cdot nH_2O$. The dianion is, in principle, a multidentate *N,O*-donor and, despite the fact that its *transoid* (not *cisoid*, as in the acid) conformation is similar in all the present systems, it does not show the same coordination mode for all the alkali metal cations.

The sodium and potassium derivatives are isomorphous, $M_2BDC\cdot 4H_2O$, Tables I and II (in which the more precise sodium complex determination is taken as exemplary of the anion) providing geometrical comparisons, the lattice and

TABLE II   Ligand geometries, $Na_2BDC\cdot 4H_2O$

Atoms	Parameter	Atoms	Parameter
Distances (Å)			
N(1)—C(2)	1.349(1)	N(1)—C(6)	1.342(1)
C(2)—C(3)	1.409(1)	C(2)—C(2^{iii})	1.490(1)
C(3)—C(31)	1.518(1)	C(3)—C(4)	1.396(1)
C(31)—O(31)	1.267(1)	C(31)—O(32)	1.257(1)
C(4)—C(5)	1.388(1)	C(5)—C(6)	1.386(1)
Angles (degrees)			
C(2)—N(1)—C(6)	118.74(7)	N(1)—C(2)—C(3)	121.98(7)
N(1)—C(2)—C(2^{iii})	115.08(7)	C(3)—C(2)—C(2^{iii})	122.87(7)
C(2)—C(3)—C(31)	125.35(7)	C(2)—C(3)—C(4)	117.84(7)
C(31)—C(3)—C(4)	116.62(7)	C(3)—C(31)—O(31)	116.23(7)
C(3)—C(31)—O(32)	118.61(7)	O(31)—C(31)—O(32)	125.05(8)
C(3)—C(4)—C(5)	120.05(7)	C(4)—C(5)—C(6)	118.08(8)
N(1)—C(6)—C(5)	123.21(8)		

The C_5N/C_5N interplanar dihedral angles are 39.79(3), 48.93(6), 41.21(6), 41.62(6)° for the Na, K, Rb, Cs adducts respectively; CCO_2/C_5N interplanar dihedral angles are 39.71(4), 36.15(7), 58.11(6), 57.60(6)° respectively. In the Na, K adducts, M, M (1 (1/2) − x, 1/2 + y, z) deviate to either side of the carboxylate plane by 1.797(2), *2.036(3)*, − 2.021(2), − 2.32(1) Å respectively.

connectivity of the sodium compound being depicted in Fig. 2. In our experience [5,19], such structural similarity of analogous sodium and potassium complexes is unusual, as it is also in, for example, biological systems, where the consequences of differences between Na^+ and K^+ arising from the considerable differences in radii can be significant and important [43]. One half of the formula unit comprises the asymmetric unit of the structure, the $M/2H_2O$ components being devoid of associations with crystallographic symmetry elements in space group *Pbcn*. One half of the anion is crystallographically independent, the midpoint of the central C—C bond being disposed on a crystallographic 2-axis parallel to *b*. The disposition of the pyridine rings is *transoid* but they are appreciably twisted from coplanarity and the pyridine planes stack, forming sheets approximately parallel to the *ac* plane about $z = 0.25$.

The carboxylate groups project to either side, their O(31) oxygen atoms bridging metal ions into columns about (0.25, *y*, 0), these in turn being linked into sheets about the $z = 0$ plane by the water molecule oxygen atoms O(1,2), and these sheets, in turn, linked to those at $z \pm 0.5$ by extended anion species. The carboxylate planes are twisted relative to their associated C_5N planes, with the metal atoms appreciably deviant to either side, carboxylate C—O bond distance pairs being essentially equivalent. There is a large angular asymmetry at their point of attachment to the ring, as there is also at the inter-ring attachment, the two adjacent substituents bowing away from each other and although the C—C(substituent) distances are not dissimilar, there is considerable difference in the associated endo-cyclic angles. The metal environments may be considered to be *tris*-chelate, one 'chelate' comprised of the pair of symmetry-related water molecule O(02)
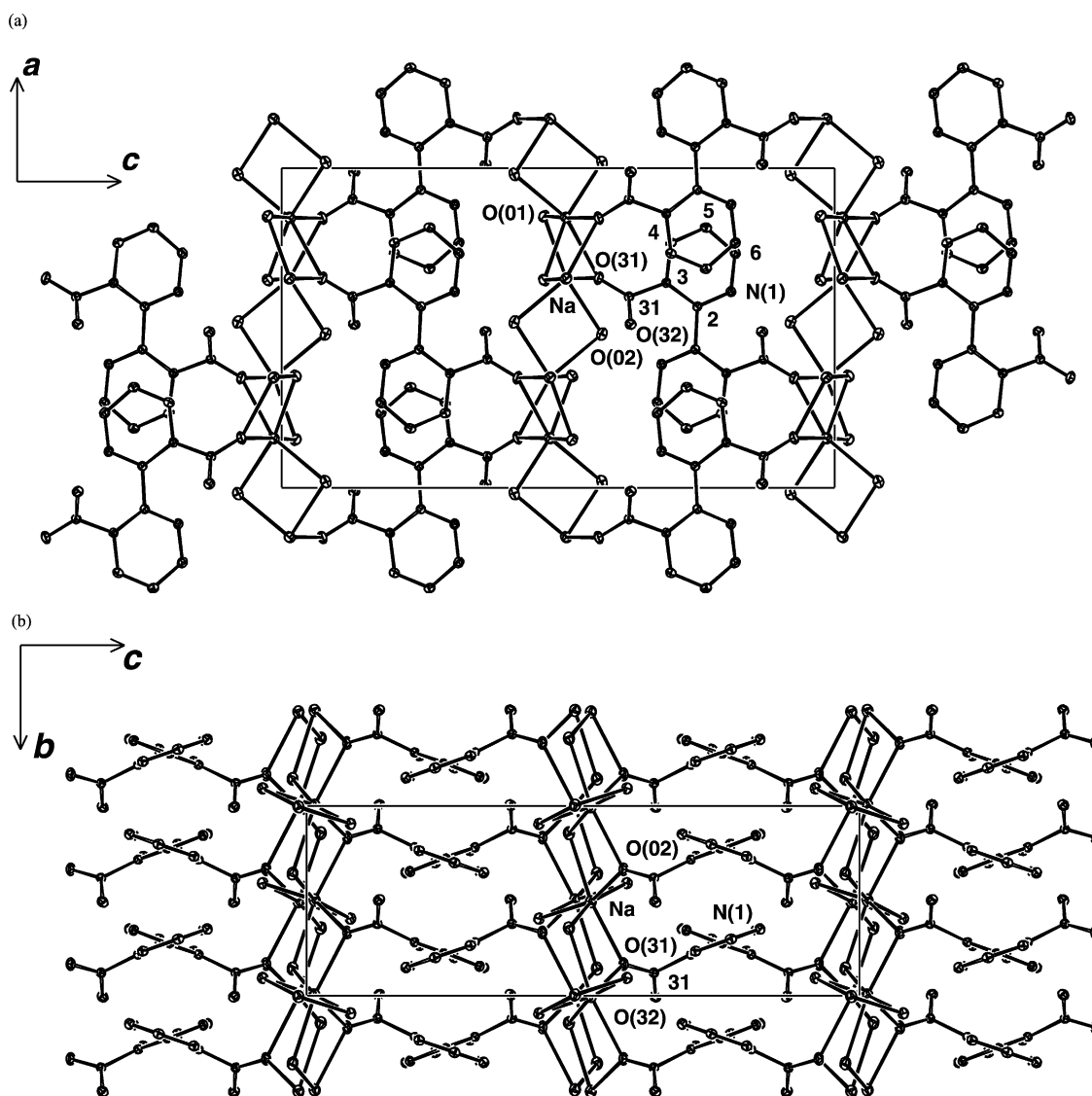

FIGURE 2   (a) Projection of the unit cell contents of $Na_2BDC \cdot 4H_2O$ down *b*. (b) Projection of the unit cell contents of $Na_2BDC \cdot 4H_2O$ down *a*.
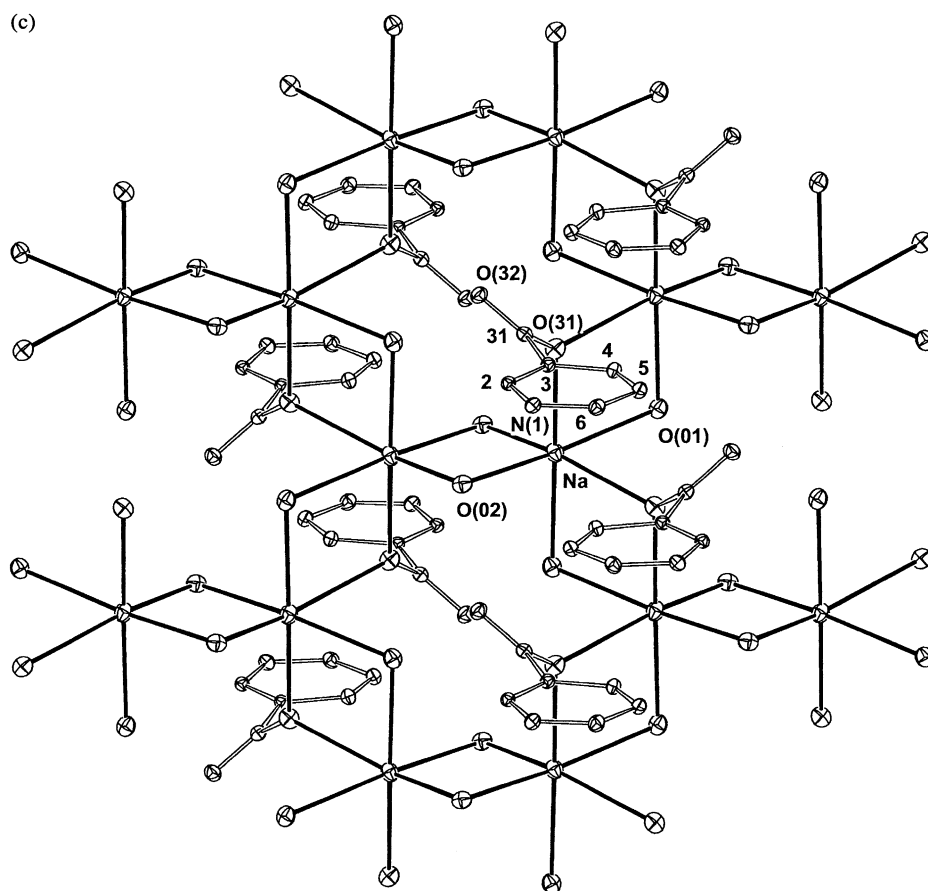
FIGURE 2 (*continued*) (c) An isolated sheet of the structure about the $z = 0$ plane.

bridging oxygen atoms, the other two of O(31)–O(01) pairs. The array is stabilised by hydrogen bonds from water molecule hydrogen atoms to carboxylate-*O* and pyridine-*N* atoms (Table II).

The rubidium and caesium compounds also form an isomorphous pair, here as monohydrates, $M_2BDC \cdot H_2O$. Again, one half of the formula unit comprises the asymmetric unit of the structure, the mid-point of the anion again disposed on a crystallographic 2-axis, as also is the water molecule oxygen atom (Fig. 3). Torsions of the *transoid* pyridine rings, and of the carboxylate units relative to their associated rings are similar to those of the lighter metal tetrahydrate species (Table II). Although the pyridine rings lie *quasi*-parallel throughout the structure, successive bipyridine systems up *a* are interleaved by lattice water molecules (Fig. 2, Table III), with closest ring atom contacts (3.7–3.9 Å) rather too long to be considered indicative of significant stacking interactions. The metal/oxygen components again aggregate into columns, the columns linked by extended anion spacers and the water molecules. The metal environments, more spacious here, are less symmetrical than those of the tetrahydrate systems, now involving some additional *N*-donor interactions. The shortest M—O distances are those involving carboxylate oxygen

atoms—the bridging O(31) and a triad of O(32)—with a M—N contact more distant and an even more distant contact to a water molecule oxygen atom which bridges two columns. These latter contacts to *N* and *O* are more nearly comparable to their counterparts in the Cs compound, the shorter M—O(carboxylate) distances expanding disproportionately.

Tautomerism in chelidamate derivatives has been frequently discussed [39,40,44,45] and, in the absence of precise hydrogen atom definition, the length of the exocyclic C(4)—O bond has been suggested [45] as the most useful structural criterion of whether the pyridone description should be accepted as more or less appropriate than that as an hydroxypyridine. In the case of chelidamic acid, H_2CHEL, itself, the length of this bond is 1.331(2) Å, consistent with the given hydroxypyridine formulation, supported by the refinement of a hydrogen atom attached to the oxygen [26]. Structure determinations of chelidamate complexes of both transition metal [44,46] and lanthanide ions [42] have generally shown close geometric similarities between bound chelidamate and dipicolinate (pyridine-2,6-dicarboxylate), leading again to assignment of an hydroxypyridine form. In all the present cases of alkali metal (and ammonium) ion complexes of the chelidamate dianion,

(a)

(b)
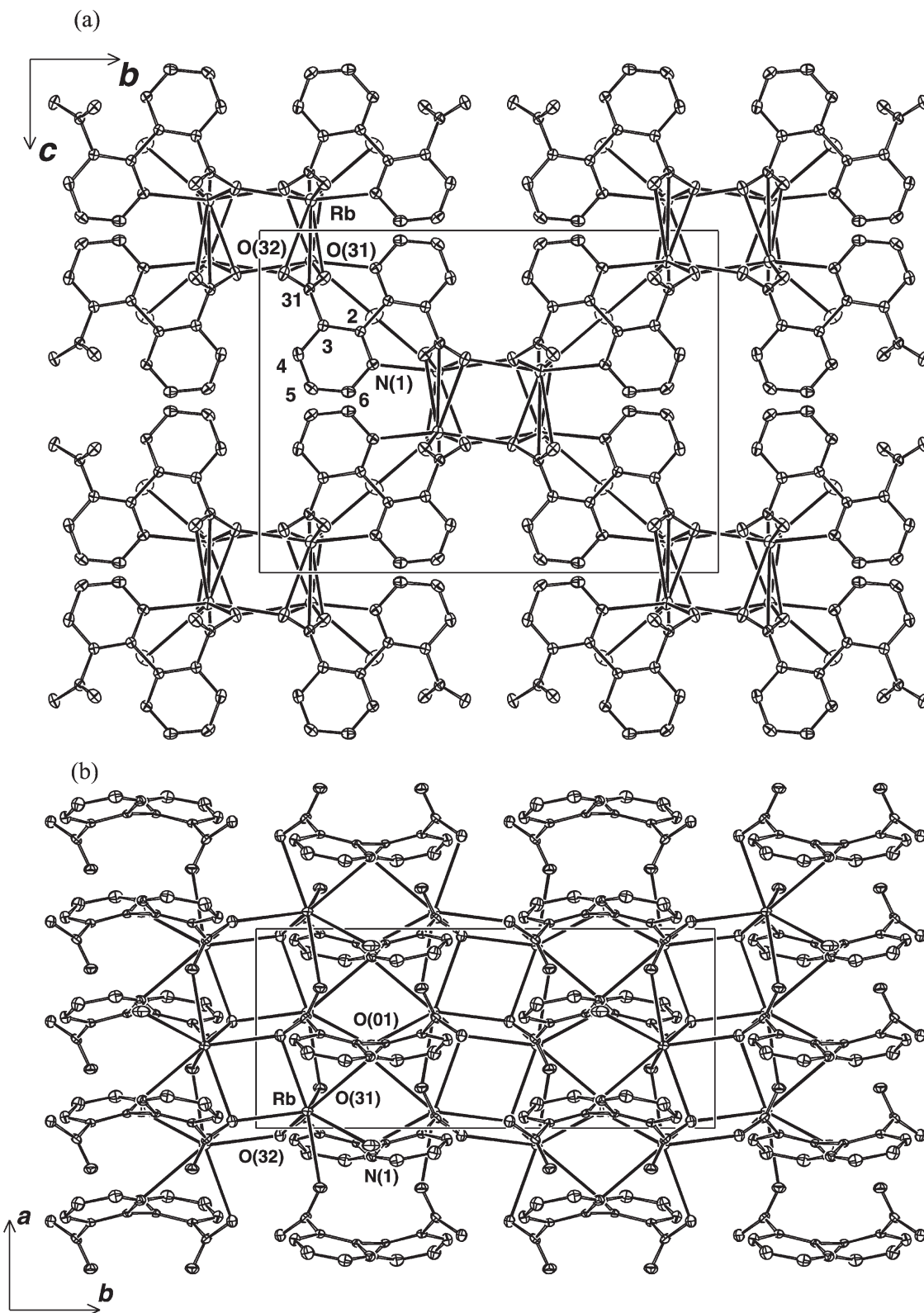
FIGURE 3   (a) Projection of the unit cell contents of Rb$_2$BDC·H$_2$O down *a*. (b) Projection of the unit cell contents of Rb$_2$BDC·H$_2$O down *b*.

however, it appears that the solid state species are better considered as pyridone derivatives.

An "isolated" chelidamate dianion may perhaps be considered as best defined in the example of the monohydrated ammonium derivative,

(NH$_4$)$_2$CHEL·H$_2$O. Here, one formula unit, devoid of crystallographic symmetry, comprises the asymmetric unit of the structure. "Proton coordination", *viz.*, hydrogen-bonding, dominates the array throughout three dimensions, although

TABLE III   Metal environments, $M_2BDC \cdot H_2O$ (M = Rb, Cs) (Presentation as in Table I; values for the *caesium* complex are given in *italics*.)

	r	O(32)	O(32^i)	O(32^{ii})	O(01^{ii})	O(32^{iii})	N(1^{iv})
O(31)	2.974(1)	44.42(4)	109.47(4)	116.78(4)	125.03(3)	85.72(4)	76.92(4)
	3.125(1)	*41.93(8)*	*108.17(3)*	*113.61(3)*	*122.08(2)*	*85.28(3)*	*74.46(3)*
O(32)	2.951(1)		77.04(4)	87.77(4)	131.90(4)	106.97(4)	120.76(4)
	3.132(1)		*78.35(3)*	*86.87(3)*	*127.55(3)*	*106.08(3)*	*116.13(3)*
O(32^i)	2.776(1)			89.98(4)	122.96(4)	76.55(4)	144.56(4)
	2.944(1)			*92.97(3)*	*125.91(3)*	*76.06(3)*	*141.29(3)*
O(31^{ii})	2.851(1)				53.01(4)	156.86(4)	119.01(4)
	3.037(1)				*50.88(4)*	*160.58(3)*	*122.10(4)*
O(01^{ii})	3.2537(9)					119.67(4)	70.28(4)
	3.3213(8)					*123.68(4)*	*75.54(4)*
O(32^{iii})	2.940(1)						69.08(4)
	3.137(1)						*65.56(3)*
N(1^{iv})	3.072(1)						
	3.221(1)						

Transformations of the asymmetric unit: i $\bar{x}, \bar{y}, \bar{z}$ ii $3/2 + x, y, \bar{z}$ iii $1/2 + x, y, \bar{z}$ iv $1/2 + x, 1/2 - y, z - 1/2$ v $x, 1/2 - y, 1/2 - z$ vi $1/2 - x, 1/2 - y, 1/2 + z$

M—O(31)—M^{iii} 92.90(4), *94.27(3)*; C(31)—O(31)—M,M^{iii} 89.6(1), 145.6(1), *91.20(9), 144.6(1)*. M—O(32)—M^i,M^{ii} 102.96(4), 91.58(4); *101.65(4), 92.21(3)*; C(31)—O(32)—M,M^{i}M^{ii} 90.8(1), 148.7(1), 106.9(1); *91.06(9), 148.1(1), 106.81(9)*; M^i—O(32)—M^{ii} 100.75(4), *101.80(3)*. M^{iii}—O(01)—M^{vi} 135.88(7), *128.78(6)*°.

the structure is largely disposed in a sheet normal to a; the short length of this oblique axis entails anion stacking, assisted by the hydrogen bonds (Fig. 4). Bonding parameters for the acid and both its ammonium and lithium (see below) derivatives are compared in Table IV, the C(4)—O(4) distance of 1.267(2) Å and the presence of a refinable hydrogen at N justifying description of the ammonium compound, in particular, as a derivative of the pyridone form of chelidamic acid. (The closest interspecies H(1)···O contact in the ammonium complex is >2.5 Å.)

In $Li_2CHEL \cdot H_2O$, one formula unit, again devoid of crystallographic symmetry, comprises the asymmetric unit of the structure, the short (b) axis of the cell being compatible with anion stacking (Fig. 5).
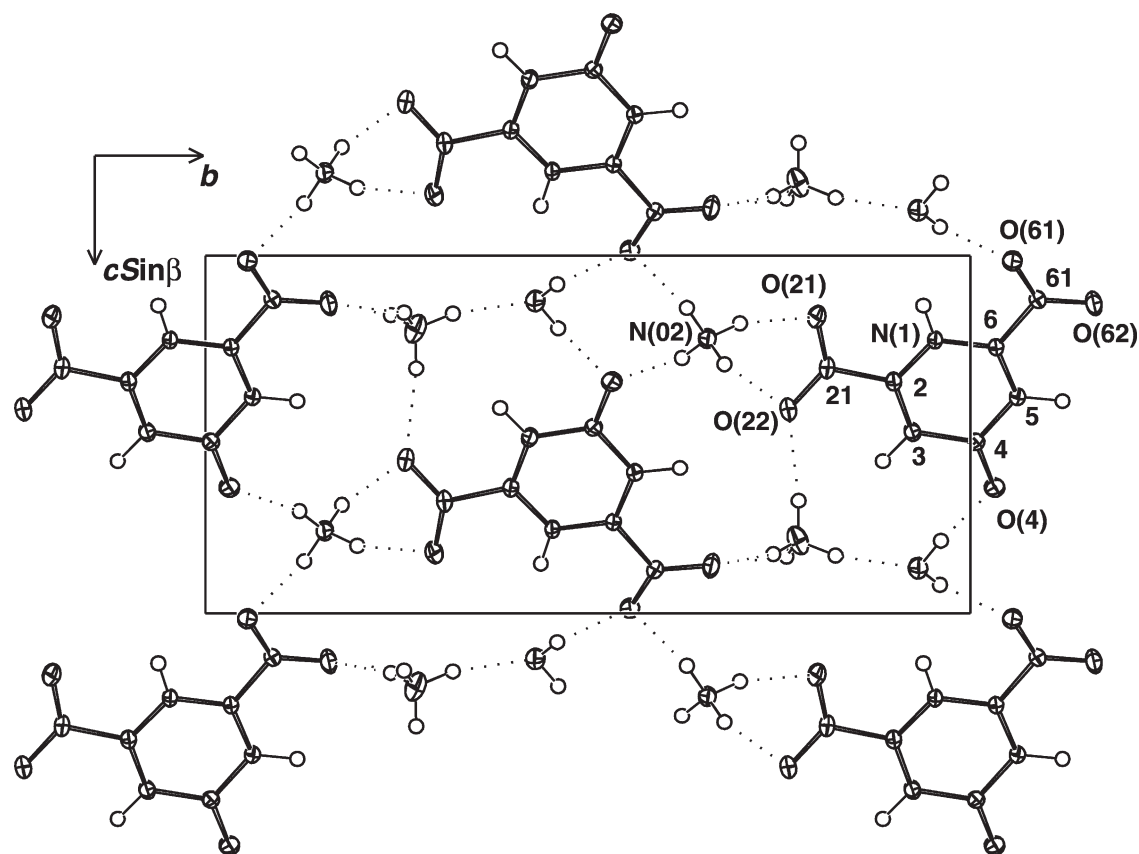

FIGURE 4   Projection of the unit cell contents of $(NH_4)_2CHEL \cdot 4H_2O$ down a.

TABLE IV Comparative geometries, H$_2$CHEL and CHEL^{2-} (in (Li$^+$)$_2$(CHEL^{2-})·3H$_2$O and (NH$_4^+$)$_2$(CHEL^{2-})·H$_2$O

Atoms	Parameter	Atoms	Parameter
Distances (Å)			
N(1)—C(2)	*1.357(2)*; 1.3585(9), 1.355(4); **1.339(2)**	N(1)—C(6)	*1.354(2)*; 1.3549(8), 1.357(5); **1.338(2)**
C(2)—C(3)	*1.378(2)*; 1.3721(8), 1.366(2); **1.396(2)**	C(5)—C(6)	*1.366(2)*; 1.3690(8), 1.366(2); **1.396(2)**
C(3)—C(4)	*1.403(2)*; 1.4315(9), 1.436(5); **1.386(2)**	C(4)—C(5)	*1.398(2)*; 1.4297(8), 1.434(4); **1.380(2)**
C(4)—O(4)	*1.331(2)*; 1.2854(8), 1.267(2); –		
C(2)—C(21)	*1.518(2)*; 1.5167(8), 1.523(5); **1.507(2)**	C(6)—C(61)	*1.510(2)*; 1.5209(8), 1.518(3); **1.505(2)**
C(21)—O(21)	*1.260(2)*; 1.2431(8), 1.250(2); **1.495(2)**	C(61)—O(61)	*1.295(2)*; 1.2425(8), 1.249(3); **1.490(2)**
C(21)—O(22)	*1.244(2)*; 1.2655(8), 1.264(4); **1.216(2)**	C(61)—O(62)	*1.221(1)*; 1.2599(8), 1.257(5); **1.215(2)**
Angles (degrees)			
C(2)—N(1)—C(6)	*120.0(1)*; 121.07(5), 121.9(2); **117.6(1)**	C(3)—C(4)—C(5)	*118.4(1)*; 116.17(5), 115.8(2); **118.9(1)**
N(1)—C(2)—C(3)	*121.2(1)*; 121.04(5), 120.3(1); **123.0(1)**	N(1)—C(6)—C(5)	*121.2(1)*; 120.58(5), 120.3(2); **123.2(1)**
N(1)—C(2)—C(21)	*117.3(1)*; 114.91(5), 115.5(2); **116.2(1)**	N(1)—C(6)—C(61)	*120.4(1)*; 116.63(5), 116.3(2); **116.5(1)**
C(3)—C(2)—C(21)	*121.4(1)*; 124.05(5), 124.2(3); **120.8(1)**	C(5)—C(6)—C(61)	*118.4(1)*; 122.69(5), 123.4(3); **120.3(1)**
C(2)—C(21)—O(21)	*115.9(1)*; 115.94(5), 116.3(3); **117.8(1)**	C(6)—C(61)—O(61)	*115.5(1)*; 115.54(5), 116.6(3); **118.6(1)**
C(2)—C(21)—O(22)	*116.2(1)*; 117.71(5), 116.9(2); **119.9(1)**	C(6)—C(61)—O(62)	*118.1(1)*; 116.75(6), 116.7(2); **119.5(1)**
O(21)—C(21)—O(22)	*127.9(1)*; 126.35(6), 126.9(4); **122.2(1)**	O(61)—C(61)—O(62)	*126.4(1)*; 127.67(6), 126.7(3); **121.9(1)**
C(2)—C(3)—C(4)	*119.2(1)*; 120.09(5), 120.8(3); **118.6(1)**	C(4)—C(5)—C(6)	*120.0(1)*; 120.82(6), 120.8(3); **118.6(1)**
C(3)—C(4)—O(4)	*119.8(1)*; 122.39(5), 122.0(3); –	C(5)—C(4)—O(4)	*121.8(1)*; 121.45(6), 122.2(3); –
θ	*23.18(5)*; 28.81(5), 8.6(2); **2.61(6)**	θ	*6.86(5)*; 22.38(4), 6.5(2); **0.63(6)**

Values for H$_2$CHEL[14] are italicised; in H$_2$CHEL, carboxylate 61 is protonated (at O(61)), as also are phenolic O(4) and the nitrogen. Also included are values for **2,6-diacetylpyridine**, for which read C(21,61) for O(21,61). θ° is the CCX$_2$/C$_5$N interplanar dihedral angle.
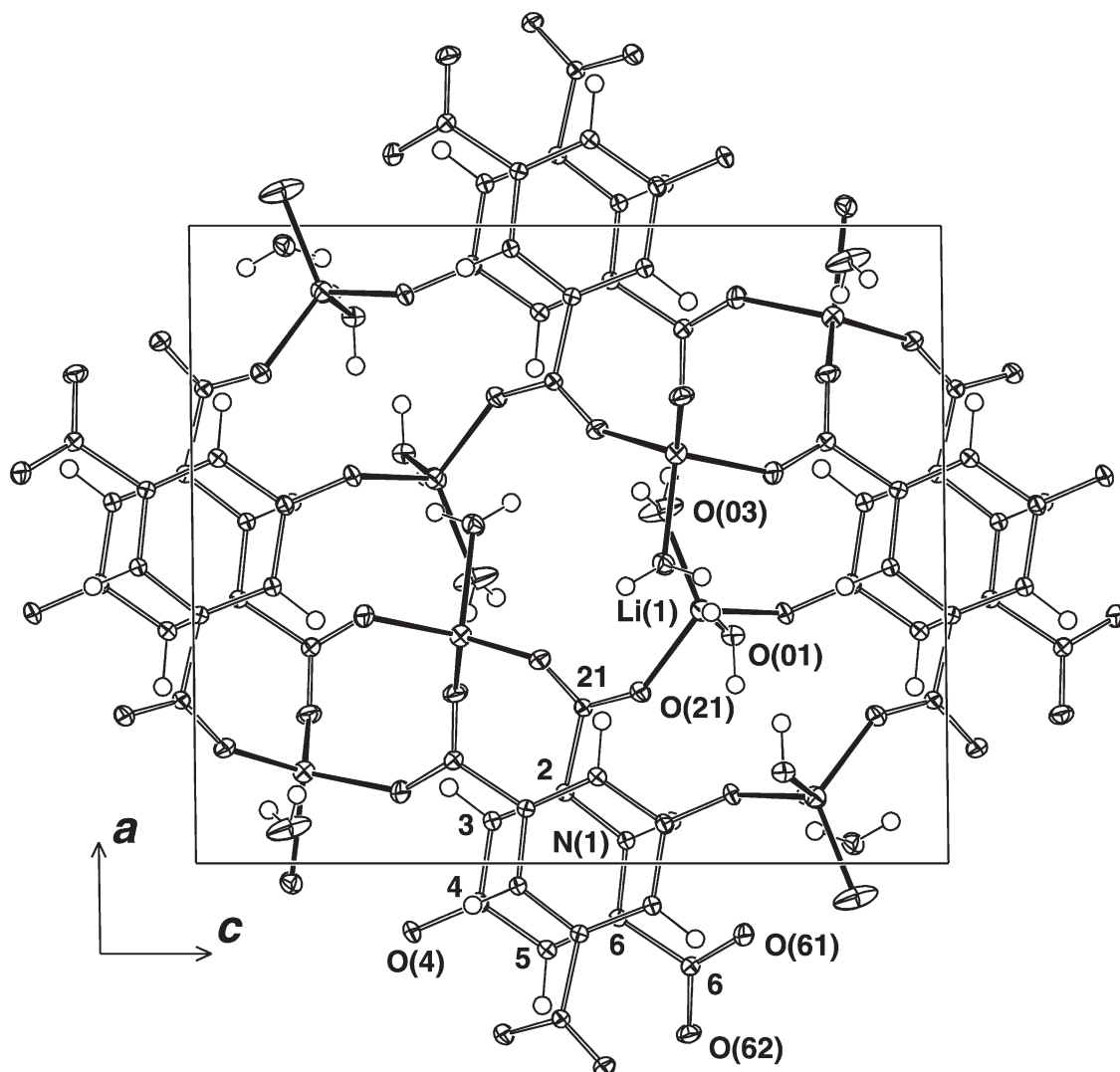

FIGURE 5 Projection of the unit cell contents of Li$_2$CHEL·3H$_2$O down *a*.

TABLE V Lithium environments, $Li_2CHEL \cdot 3H_2O$ (Presentation as for Table I.)

	(a) Li (1)					(b) Li (2)			
Atom	r	O(03)	O(21)	O(4^i)	Atom	r	O(22)	O(62^{ii})	O(61^{iii})
O(01)	1.933(1)	107.46(7)	111.18(7)	114.39(7)	O(02)	2.006(1)	107.44(6)	106.21(7)	92.15(6)
O(03)	1.881(1)		118.73(7)	108.03(7)	O(22)	1.920(1)		119.28(7)	112.38(7)
O(21)	1.925(1)			96.99(6)	O(62^{ii})	1.913(1)			115.19(7)
O(4^i)	1.950(1)				O(61^{iii})	1.902(1)			

Li(2)—O(21)—C(21) 145.46(6); Li(2)—O(22)—C(21) 151.18(6); C(4)—O(4)—Li(1^{iv}) 136.20(6); C(61)—O(61)—Li(2^v) 142.88(6); C(61)—O(62)—Li(2^{ii}) 142.80(6)°.

Transformations of the asymmetric unit: i $1/2 + x, 1/2 - y, 1/2 + z$ ii $\bar{x}, \bar{y}, 1 - z$ iii $1/2 + x, 1/2 - y, z - 1/2$
 iv $x - 1/2, 1/2 - y, z - 1/2$ v $x - 1/2, 1/2 - y, 1/2 + z$

N-protonation and a C(4)—O(4) distance of 1.2854(8) Å again indicate the pyridone formulation to be appropriate (Table IV). The anions are linked by four-coordinate Li atoms, both as successive members up a stack and at the same level within the unit cell, the latter connectivity giving rise to a 26-membered ring. Unlike the ammonium compound, the lithium complex has a structure in which the ring NH unit, as well as the water molecules and carboxylate groups, participates in the hydrogen bond network (see below, Tables V, VIII).

The structure of the sodium complex, formulated from the structure solution as $Na_5(HCHEL)_3$ CHEL$\cdot \sim 28.6H_2O$ or $[Na_5(HCHEL)_3CHEL(OH_2)_{10}]$ $\sim 18.6H_2O$, is less readily interpreted. (Note that numerous efforts were made to obtain a material of 2:1 Na:CHEL stoichiometry but the only crystalline material resulting appeared always to be of this "unusual" composition.) A considerable component of the lattice water array (and, perhaps, associated protons) is disordered and not clearly defined, forming sheets about the ab faces of the cell which sandwich the complex component, itself a sheet disposed about $z = 0.5$ (Fig. 6). The C(n4)—O(n4) distances (1.266(4), 1.271(4) Å) and N-protonation once more indicate the ligand to be in its pyridone form. The complex may be regarded as growing out of a string of sodium atoms, Na(1), lying on crystallographic inversion centres at the centres of successive bc faces and spaced by the unit a translation. Like the other Na atoms, these Na are six-coordinate and essentially octahedral, bridging between the two sets involving water molecule oxygen atoms O(12) and carboxylate 12, Na(2,3) being linked directly by carboxylate 22 and indirectly in adjacent cells by carboxylate 26. Water molecule oxygen atoms O(3) about Na(2) and O(4,5) about Na(3) are terminal. The aromatic ring planes are

TABLE VI Sodium environments, $Na_5CHEL_4 \cdot 28.6H_2O$ (Presentation as in Table I.)

(a) Na(1) (centrosymmetric), Na(1)—O(122,1,2) are 2.441(3), 2.452(2), 2.454(3) Å; O(122)—Na(1)—O(1,2), O(1)—Na—O(2) are 93.15(8), 100.8(1), 102.20(8)°.

(b) Na(2)

Atom	r	O(3)	O(121)	O(221)	O(162^i)	O(261^{ii})
O(2)	2.412(3)	160.5(1)	80.7(1)	96.3(1)	100.3(1)	79.62(9)
O(3)	2.396(3)		87.7(1)	95.3(1)	95.3(1)	85.17(9)
O(121)	2.305(3)			176.9(1)	90.08(9)	91.68(9)
O(221)	2.286(3)				89.89(9)	88.34(9)
O(161^i)	2.436(3)					178.2(1)
O(261^{ii})	2.544(2)					

(c) Na(3)

Atom	r	O(5)	O(1^{iii})	O(221)	O(222)	O(262^{iv})
O(4)	2.356(3)	115.6(1)	83.6(1)	121.1(1)	79.8(1)	94.5(1)
O(5)	2.330(3)		159.0(1)	96.7(1)	87.8(1)	80.6(1)
O(1^{iii})	2.408(3)			78.82(9)	104.7(1)	89.98(9)
O(221)	2.654(3)				52.29(9)	140.7(1)
O(222)	2.393(2)					163.4(1)
O(262^{iv})	2.367(2)					

Transformations of the asymmetric unit: i $\bar{x}, \bar{y}, 1 - z$ ii $1 - x, \bar{y}, 1 - z$ iii $1 + x, y, z$ iv $x, 1 + y, z$
 v $x, y - 1, z$ vi $x - 1, y, z$
Na(2)—O(121)—C(121) 163.2(2); Na(1)—O(122)—C(121) 107.3(2); Na(2^i)—O(161)—C(161) 114.7(2);
C(221)—O(221)—Na(2,3) 165.6(2), 83.1(3); Na(2)—O(221)—Na(3) 97.91(9); Na(3)—O(222)—C(221) 95.0(2);
C(261)—O(261)—Na(2^{ii}) 105.2(2); C(261)—O(261)—Na(3^v) 161.1(2); Na(1)—O(1)—Na(3^{vi}) 126.6(1);
Na(1)—O(2)—Na(2) 107.0(1)°.

TABLE VII Potassium environments, $K_8(CHEL)_4 \cdot 6H_2O$ (Presentation as in Table I.)

(a) K(1)

	r	O(24^i)	O(122)	O(122^{ii})	O(262^{iv})	O(262^{iii})
KO(24)	2.675(3)	86.96(7)	142.42(9)	80.87(7)	81.50(8)	139.47(8)
O(24^i)	2.677(2)		83.11(8)	143.35(9)	138.45(8)	79.28(8)
O(122)	2.643(3)			85.82(7)	127.88(8)	73.67(8)
O(122^{ii})	2.765(2)				73.69(8)	130.30(7)
O(262^{iv})	2.690(3)					84.06(8)
O(262^{iii})	2.809(3)					

(b) K(2)

	r	O(14^i)	O(222)	O(222^i)	O(162^v)	O(162^{vi})
O(14)	2.680(3)	87.17(8)	143.70(9)	82.13(7)	79.21(8)	137.56(8)
O(14^{ii})	2.662(2)		83.19(8)	143.88(9)	137.06(8)	78.78(8)
O(222)	2.697(3)			85.36(7)	129.47(8)	74.34(8)
O(222^i)	2.736(2)				74.39(8)	130.26(7)
O(162^v)	2.721(3)					84.38(8)
O(162^{vi})	2.762(3)					

(c) K(3)

	r	O(44^{ii})	O(322)	O(322^i)	O(462^{vii})	O(462^{viii})
O(44)	2.638(3)	88.34(8)	143.6(1)	82.12(7)	85.03(9)	145.15(8)
O(44^{ii})	2.647(3)		87.28(8)	146.01(9)	143.51(9)	80.85(9)
O(322)	2.679(3)			81.62(7)	118.09(8)	69.20(8)
O(322^i)	2.947(2)				68.20(8)	123.70(8)
O(462^{vii})	2.634(3)					84.38(9)
O(462^{viii})	2.844(3)			(K(3)...O(3) 3.303(3) Å)		

(d) K(4)

	r	O(34^i)	O(422)	O(422^{ii})	O(362^{ix})
O(34)	2.677(3)	86.79(8)	133.14(9)	76.90(7)	140.07(8)
O(34^i)	2.683(3)		77.00(8)	133.31(9)	80.04(9)
O(422)	2.772(3)			83.02(7)	80.20(8)
O(422^{ii})	2.784(2)				137.27(8)
O(362^{ix})	2.778(3)			(K(4)...O(2) 3.313(3) Å)	

(e) K(5)

	r	O(5)	O(5^{ii})	O(321)	O(321^i)	O(261^{iii})
O(3)	2.693(3)	78.21(9)	80.35(9)	84.78(9)	82.36(9)	140.24(9)
O(5)	2.817(3)		82.51(9)	162.99(7)	95.47(8)	67.89(8)
O(5^{ii})	2.768(3)			95.20(8)	162.64(7)	113.80(8)
O(321)	2.846(2)				81.69(8)	127.58(8)
O(321^i)	2.785(3)			(K(5)...O(6^{iii}) 3.221(3) Å)		80.87(7)
O(261^{iii})	2.781(2)			(K(5)...O(261^{iv}) 3.031(3) Å)		

(f) K(7)

	r	O(1)	O(1^{ii})	O(421^{viii})	O(421^{vii})	O(161^i)
O(2)	2.755(3)	88.35(10)	72.58(9)	76.98(9)	92.47(9)	125.08(10)
O(1)	2.762(3)		82.98(9)	165.15(7)	96.53(9)	67.71(8)
O(1^{ii})	2.796(3)			94.65(8)	165.04(7)	114.44(8)
O(421^{viii})	2.832(3)				81.98(8)	125.94(8)
O(421^{vii})	2.782(3)			(K(7)...O(4) 3.232(4) Å)		78.77(7)
O(161)	2.789(2)			(K(7)...O(161^{ii}) 3.008(3) Å)		

(g) K(8)

	r	O(2^{vi})	O(221)	O(221^i)	O(361^{iii})	O(361^{iv})
O(6)	2.779(4)	151.56(9)	66.72(8)	104.11(9)	100.22(8)	62.69(9)
O(2^{vi})	2.786(3)		134.73(9)	98.5(1)	58.71(8)	93.35(9)
O(221)	2.870(3)			81.24(8)	166.47(9)	94.96(8)
O(221^i)	2.786(3)				99.40(8)	166.52(8)
O(361^{iii})	2.771(3)			(K(8)...O(6^i) 3.348(4) Å)		81.29(8)
O(361^{iv})	2.881(3)			(K(8)...O(1^{vi}) 3.155(3) Å)		

(h) K(6)

	r	O(3)	O(121)	O(121^{ii})	O(461^{viii})	O(461^{vii})
O(4)	2.817(5)	136.1(1)	65.3(1)	102.8(1)	99.6(1)	60.9(1)
O(3)	2.718(4)		119.8(1)	120.9(1)	74.54(9)	75.21(9)
O(121)	2.704(3)			83.16(8)	163.9(1)	91.78(9)
O(121^{ii})	2.843(3)				95.64(9)	163.4(1)
O(461^{viii})	2.711(3)			(K(6)...K(6′) 1.012(9) Å)		78.77(7)
O(461^{vii})	2.746(3)			(K(6)...O(4^{ii},5,5^{ii}) 3.380(4), 3.361(3), 3.426(3) Å)		

(i) K(6′)

	r	O(4)	O(121^{ii})	O(121)	O(461^{vii})	O(461^{viii})
O(4^{ii})	2.810(9)	100.1(4)	65.3(2)	132.9(3)	132.2(3)	60.8(2)
O(4)	1.938(9)		127.5(4)	76.0(3)	73.3(3)	126.9(3)
O(121^{ii})	2.854(8)			80.0(2)	154.1(4)	91.1(2)
O(121)	2.875(7)				92.5(4)	154.4(4)
O(461^{vii})	2.680(8)					85.1(2)
O(461^{viii})	2.765(8)					

Transformations of the asymmetric unit: i $x-1; y, z$ ii $x+1, y, z$ iii $1-x, \bar{y}, \bar{z}$ iv $2-x, \bar{y}, \bar{z}$ v $\bar{x}-1, 1-y, \bar{z}$ vi $\bar{x}, 1-y, \bar{z}$ vii $\bar{x}, 1-y, 1-z$ viii $1-x, 1-y, 1-z$

Note that K(x)...K(x^{i,ii}) are all 3.683(1) Å.

TABLE VIII   Hydrogen-bonding in the chelidamates

Atoms	Distances (Å)	Atoms	Distances (Å)
(a) The ammonium salt			
N(01),H(01a)...O(03)	2.750(5), 1.87(3)	N(02),H(02a)...O(21)	2.843(5), 1.96(2)
H(01b)...O(22^i)	2.899(4), 2.02(3)	H(02b)...O(22^{iv})	2.899(4), 2.03(2)
H(01c)...O(62^{ii})	2.802(4), 2.09(3)	H(02c)...O(61^v)	2.836(2), 1.94(2)
H(01d)...O(62^{iii})	2.768(4), 1.90(3)	H(02d)...O(4^{iii})	2.781(4), 1.94(2)
O(03),H(03a)...O(61)	2.831(4), 2.07(3)		
H(03b)...O(4^{iii})	2.711(4), 1.85(6)		

Transformations of the asymmetric unit: I $x+1, y, z$ ii $2-x, y-1/2, 1-z$ iii $1-x, y-1/2, 1-z$ iv $x-1, y, z$
   v $\bar{x}-1, y-1/2, \bar{z}$ vi $2+x, y, 1+z$

Atoms	Distances (Å)	Atoms	Distances (Å)
(b) The lithium salt			
N(1),H(1)...O(01^I)	2.9903(7), 2.16(1)	O(02),H(02a)...O(22^{iv})	2.8876(7), 2.06(1)
O(01),H(01a)...O(02^{ii})	2.8667(8), 2.03(1)	H(02b)...O(4^v)	2.8482(7), 1.96(1)
H(01b)...O(4^{iii})	2.7908(7), 1.92(1)	O(03),H(03a)...O(22^{vi})	2.8875(9), 2.07(2)
		H(03b)...O(62)	2.7960(9), 1.95(2)

Transformations of the asymmetric unit: I $x+1, y, z$ ii $2-x, y-1/2, 1-z$ iii $1-x, y-1/2, 1-z$ iv $x-1, y, z$
   v $\bar{x}-1, y-1/2, \bar{z}$ vi $2+x, y, 1+z$

Atoms	Distances (Å)	Atoms	Distances (Å)
(c) [Na$_5$CHEL$_4$(OH$_2$)$_{10}$]·18.6H$_2$O			
O(1),H(1a)...O(161^i)	2.830(3), 1.99(4)	O(4),H(4a)...O(162^{ii})	2.880(4), 1.89(5)
H(1b)...O(261^i)	2.874(4), 2.09(4)	H(4b)...O(122^{iv})	2.840(3), 2.00(5)
O(2),H(2a)...O(262^{ii})	2.884(4), 2.10(6)	O(5),H(5a)...O(122^v)	2.947(4), 1.88(7)
H(26)...O(262^{iii})	2.829(4), 2.07(5)	H(5b)...O(162^v)	2.832(4), 1.95(6)
O(3),H(3a)...O(261)	2.841(3), 2.03(6)		
H(3b)...O(161)	3.078(4), 2.28(7)		

Transformations of the asymmetric unit: i $\bar{x}, \bar{y}, 1-z$ ii $1-x, \bar{y}, 1-z$ iii $x, 1+y, z$ iv $1-x, 1-y, 1-z$ v $\bar{x}, 1-y, 1-z$

approximately normal to a, forming interleaving stacks up a. Hydrogen bonds may be identified with reasonable certainty insofar as they involve water molecules associated with the core polymer (Table VIII). Beyond that, at the interface of the polymer with the disorderly solvent layer and within that layer, questions of the degree and location of protonation become much more speculative. Indeed, the totality of the structure is reminiscent of layers of membranes separated by a more mobile phase, with the possibilities of conduction both along the mobile phase and by deposition of charge at one membrane surface with compensating release at the other.

The stoichiometry of the potassium complex is ostensibly more clearly defined as K$_8$CHEL$_4$·6H$_2$O, one half of the formula unit comprising the asymmetric unit of a similarly complicated structure (Fig. 7). All hydrogen atoms associated with the anions were located and refined, N-protonation again being apparent and, in conjunction with C(4)—O(4) distances of 1.256(4), 1.255(4), 1.262(4) and 1.263(4) Å, being taken as indicative of pyridone forms for the ligands. Again, a short axis is found, the ligand ring planes *quasi*-normal to and stacking up it, with the structure forming a two-dimensional web slanting through the cell and linking in the third dimension to others to each side in a. The structure can be seen as incorporating a number of motifs. One is that of the anions, all being disposed with their O(4) atoms almost within the ab plane, linking to potassium alternately to either side along b, similarly at $z = 0.5$. Successive pairs of anions thus disposed bond to the associated potassium atoms

through their carboxylate groups to form 14-membered rings lying across $z = 0$, 0.5. The potassium atoms involved thus are K(1–4), all with *quasi*-trigonal-prismatic geometries, still essentially six-coordinate (most have a couple of longer contacts). A second set of four potassium atoms, K(5–8), are found lying in the plane at $z = 0.25$, interacting with carboxylate groups only from the anions. They also thus form macrocyclic rings about $z \sim 0.25$ along the b direction, alternately containing two and four potassium atoms, yielding, in both cases, 16-membered rings, the one type not encompassing the ligand ring and its nitrogen, the other with both of these. These two types of rings are bridged, through the K atoms at $z \sim 0.25$, by water molecule oxygen atoms, one in the K$_2$ rings and two in the K$_4$. Although seemingly μ_2-O in nature, "contacts" to third K atoms are also found at various distances suggestive of weaker interactions to the trigonal prismatic K(1–4) atoms, with some variability in the environments of K(5–8). This variability is possibly concomitant upon some incompatibility in the energetics associated with the array of the 14-membered macrocycles associated with K(1–4) only, which are well ordered by comparison with the larger macrocycles involving K(5–8), culminating in disorder of K(6), modelled as distributed over a pair of sites, 1.012(9) Å apart, of disparate occupancies. Indeed, one may question whether the smaller component of K(6) may be an impurity in the lattice comprising an appropriate H$_3$O$^+$/H$_2$O composite. Hydrogen atoms being located and refined in association with the CHEL ligands only, we do not
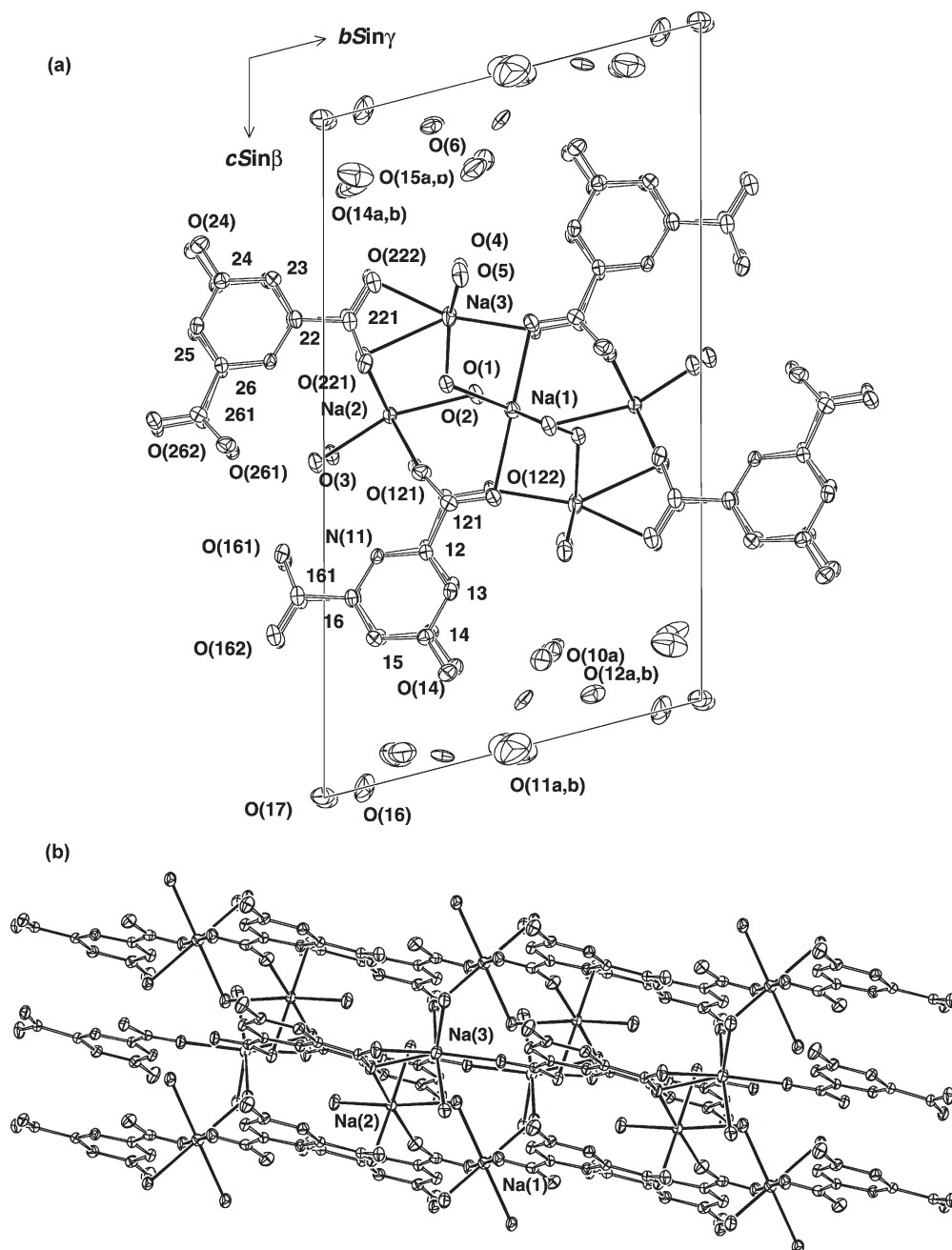
FIGURE 6   (a) Unit cell contents of $[Na_5CHEL(CHELH)_3(OH_2)_{10}]\cdot18.6H_2O$ down *a*. (b) The sheet of the complex about the $z = 0.5$ plane.

indulge in speculation regarding that or H-bonding schemes between these ligands and to the water molecules, except to note that the NH groups have close interspecies contacts.

The rubidium and caesium complexes are more difficult of access experimentally, the first comprised of fine hairs of marginal substance, and the second, more substantial but still small, and twinned, militating against the acquisition of data of sufficient quality to permit hydrogen atom refinement. The structure once more is simple (Fig. 8), accommodated again in a cell with a 4 Å

axis, *cf* the ammonium complex, one anhydrous formula unit comprising the asymmetric unit. Again, the structure may be viewed essentially as a two-dimensional web, inclined to the *bc* plane, the size and high coordination number of the cation resulting in linking of adjacent planar components by interplanar Cs$\cdots$O interactions. While carboxylates 21,61 are, unsurprisingly, chelate to (different) Cs(2), O(21,61) also behave as a chelate of considerably larger bite (enclosing protonated N(1)), of Cs(1); all carboxylate oxygen atoms are involved in coordination to at
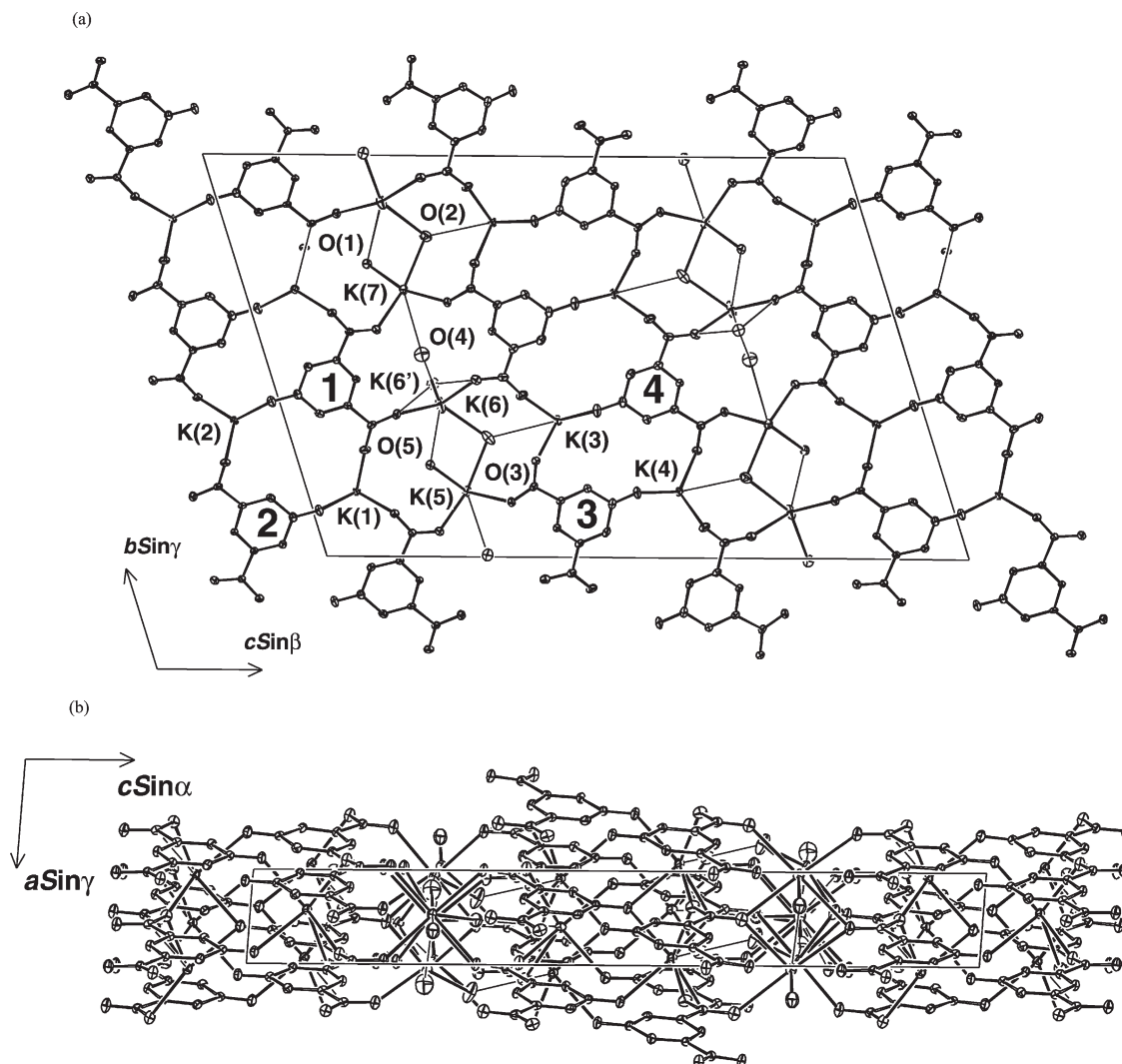
(a)

(b)

FIGURE 7   (a) Unit cell contents of $K_8CHEL_4\cdot6H_2O$ projected down a. (b) Unit cell contents of $K_8CHEL_4\cdot6H_2O$ projected down b.

least two Cs atoms (depending on the distance considered to constitute an 'interaction') (Table IX), while O(4) bridges a pair separated by the a translation.

The results of the X-ray study, albeit of modest precision, establish with reasonable certitude the rubidium complex to be modelled as Rb_3 (CHEL)(HCHEL)$\cdot6H_2O$; all oxygen atoms are associated with rubidium atoms either unidentate or bridging. Within ligand n, the carboxylate planes are quasi-coplanar with the C_5N ring, O(n21,n61) lying adjacent to the nitrogen on either side, O(n21,n62) bridging, O(n61,n22) unidentate, while water molecule oxygens O(03–05) are terminally bound and O(01,02,06) bridging. Thus all oxygen atoms are bound to (eight-coordinate) rubidium atoms with the above interactions 2.846(7)– 3.236(7) Å, excepting O(n4). The latter confront each other, O(14)$\cdots$O(24) $(1 - x, \; 0.5 + y, \; 0.5 - z)$ being

2.41(1) Å; O(14) is assigned as protonated, but that is equivocal, the only non-trivial difference in the ligand bonding distances being C(04)—O(n4), 1.31(1), 1.28(1) Å $(n = 1, 2)$, so that ligand 2 is tentatively assigned as 4-pyridone-2,6-dicarboxylate, and ligand 1 the monoprotonated counterpart. The C_5N planes of the two ligands lie closely parallel to each other (interplanar dihedral angle 5.4(3)°) and to the bc plane and to their associated $C\cdot CO_2$ carboxylate planes (dihedrals of associated planes 12, 16 to $C_5N(1)$ 1.9, 6.1(4)° and 22, 26 to $C_5N(2)$ 0.5(3), 6.4(4)°) and, given the length of a (7.044(3) Å), their stacking up that axis may be considered a significant motif in the structure (Fig. 9(a)); two independent stacks are found, derivative of ligands 1,2 respectively. To either side, their carboxylate substituents link successive Rb(2), Rb(3) respectively in the c (and also, columnwise, in the a dimension), with Rb(1) between them in the b (and also the a)
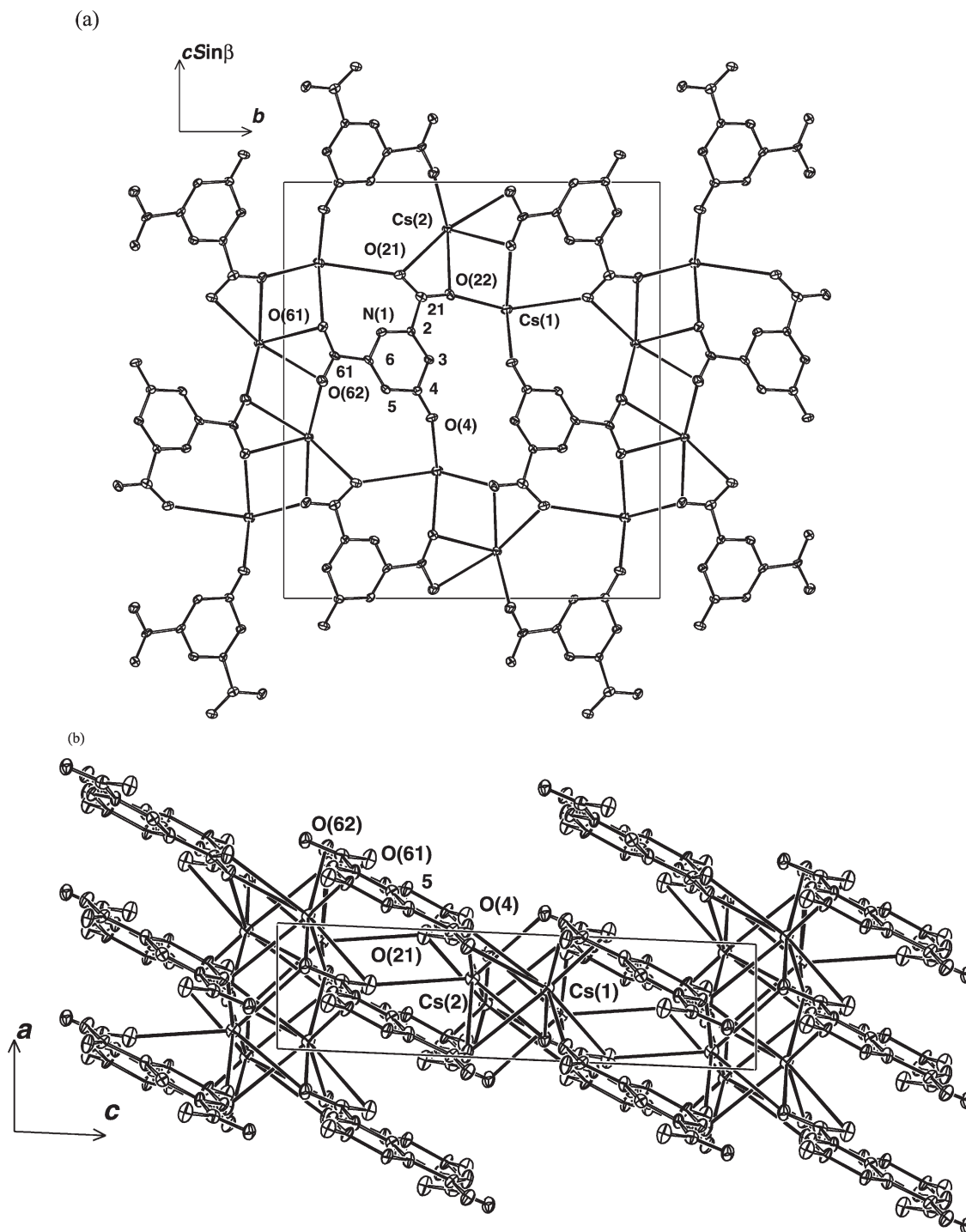
(a)

(b)

FIGURE 8   (a) Unit cell contents of Cs₂CHEL, projected down *a*. (b) Unit cell contents of Cs₂CHEL, projected down *b*.

dimension, so that a three-dimensional lattice with nodes at the rubidium atoms results; Rb(1)$\cdots$Rb(2,3) are 4.142(2), 4.164(2), Rb(2)$\cdots$Rb(2) ($\bar{x}$, $\bar{y}$, $\bar{z}$; $\bar{x}-1$, $\bar{y}$, $\bar{z}$) 4.442(2)(×2) and Rb(3)$\cdots$Rb(3) ($1-x$, $\bar{y}$, $1-z$; $\bar{x}$, $\bar{y}$, $1-z$) 4.626(2), 4.847(2) Å. The latter observation, that successive inversion-related Rb(2), Rb(3) in their columns up *a* are equally and unequally spaced respectively is a point of some interest.

Consideration of the three rubidium environments in Table X show, firstly, as evident from Fig. 9(b) (which shows a less complex slice of the cell, bounded by *z ca* 0.25–0.75, *y ca* −0.125–0.375, *x ca* 0–1) the approximate 2-symmetry of the Rb(1) environment. This extends outwards to either side to Rb(2,3), which have closely similar sections of their coordination spheres defined by three water molecule oxygens,

TABLE IX   The caesium environments, Cs_2CHEL, presentation as in Table I

(a) Cs(1)

Atom	r	O(22^i)	O(4^{ii})	O(4^{iii})	O(61^{iv})	O(21^v)	O(61^v)
O(22)	3.052(5)	80.1(1)	128.6(2)	76.4(2)	102.0(1)	132.2(3)	57.6(1)
O(22^i)	3.131(5)		75.8(2)	129.8(1)	62.4(1)	137.4(1)	110.0(1)
O(4^{ii})	2.916(6)			85.3(2)	105.7(2)	94.4(1)	172.9(1)
O(4^{iii})	2.962(6)				166.3(1)	89.4(1)	93.7(1)
O(61^{iv})	3.033(6)					81.7(1)	74.4(1)
O(21^v)	3.313(6)						78.6(1)
O(61^v)	3.519(6)						

(b) Cs(2)

Atom	r	O(22)	O(21^i)	O(22^i)	O(62^{vi})	O(62^{vii})	O(61^{iv})	O(62^{iv})	O(61^v)
O(21)	3.458(6)	39.7(1)	73.2(2)	92.4(1)	135.6(1)	84.9(1)	134.4(1)	161.6(1)	85.8(1)
O(22)	3.092(5)		79.0(1)	73.0(1)	165.0(1)	110.0(2)	96.1(1)	126.3(1)	59.3(1)
O(21^i)	3.209(6)			38.3(1)	86.0(1)	132.0(1)	91.3(1)	120.3(2)	133.1(1)
O(22^i)	3.569(5)				94.7(1)	170.0(1)	55.5(1)	92.8(1)	104.1(1)
O(62^{vi})	3.172(5)					80.7(2)	83.4(1)	61.5(1)	134.0(1)
O(62^{vii})	2.969(8)						132.0(1)	92.8(1)	85.3(1)
O(61^{iv})	3.267(6)							40.6(1)	74.1(1)
O(62^{iv})	3.236(6)								75.8(1)
O(61^v)	3.341(5)								

Transformations of the asymmetric unit: i $x-1, y, z$ ii $1-x, 1-y, 1-z$ iii $2-x, 1-y, 1-z$
iv $x-1\,1/2, 1/2-y, 1/2+z$ v $x-1/2, 1/2-y, 1/2+z$ vi $1\,1/2-x, y-1/2, 1/2-z$ vii $2\,1/2-x, y-1/2, 1/2-z$
Cs(1)...Cs(2) is 4.0384(7), Cs(1)...Cs(1^i) = Cs(2)...Cs(2^i) 3.9806(6) (=a) Å. Dihedral angles of CCO_2 planes 2, 6 to the C_5N plane are 6.9(3), 2.6(3) Å. C(4)—O(4) is 1.252(8) Å.

two terminally bound, the other bridging to Rb(1), and a chelating carboxylate associated with the companion ligand of the asymmetric unit. Beyond this, however, the quasi-symmetry breaks down, by virtue of the ligand dispositions, most readily apprehended by consideration (e.g.) of the relation of pairs of ligands which bridge successive rubidiums in the columns up a, these linking Rb(2) being related a

glide lying oblique to each other, while those linking Rb(3) are inversion related and therefore parallel.

Analysis of Lattice Interactions

The primary coordination spheres found for the metals in the present complexes are evident in Figs 1–8. In the general context of alkali metal ion

TABLE X   The rubidium environments, $Rb_3(CHEL)(HCHEL) \cdot 6H_2O$ (Presentation as in Table I.)

(a) Rb(1)

Atom	R	O(01)	O(06)	O(121)	O(221)	O(161^i)	O(261^{ii})
O(05)	2.87(1)	149.1(3)	138.5(2)	84.8(3)	80.1(3)	80.9(3)	73.9(3)
O(01)	2.960(7)		72.4(2)	75.1(2)	115.6(2)	72.0(2)	132.9(2)
O(06)	3.297(7)			118.7(2)	77.4(2)	134.8(2)	68.0(2)
O(121)	2.846(7)				163.5(2)	77.2(2)	102.6(2)
O(221)	2.904(7)					93.9(2)	79.5(2)
O(121^i)	2.889(7)						154.7(2)
O(261^{ii})	2.879(7)						

(b) Rb(2)

Atom	r	O(01)	O(03)	O(121)	O(122)	O(122^{iv})	O(162^{ii})	O(162^v)
O(02^{iii})	3.236(7)	95.3(2)	63.6(2)	75.1(2)	118.1(2)	102.0(2)	65.1(2)	171.3(2)
O(01)	2.936(7)		75.4(2)	72.8(2)	73.9(2)	139.9(2)	145.4(2)	86.2(2)
O(03)	2.929(8)			124.3(2)	149.2(2)	80.4(2)	115.2(2)	109.1(2)
O(121)	3.027(7)				43.1(2)	146.6(2)	74.6(2)	113.0(1)
O(122)	3.099(7)					125.6(2)	90.1(2)	70.2(2)
O(122^{iv})	2.853(7)						74.2(2)	72.2(2)
O(162^{ii})	2.865(7)							117.5(2)
O(162^v)	2.898(7)							

(c) Rb(3)

Atom	r	O(06)	O(04)	O(221)	O(222)	O(222^{iv})	O(262^{ii})	O(262^{vii})
O(02)	3.048(7)	107.2(2)	67.5(2)	75.3(2)	117.7(2)	152.1(2)	70.9(2)	125.2(2)
O(06)	3.241(8)		77.6(2)	77.0(2)	73.7(2)	52.6(2)	148.4(2)	126.1(2)
O(04)	2.905(7)			125.4(2)	151.0(2)	87.6(2)	126.2(2)	109.4(2)
O(221)	2.998(8)				43.3(2)	112.5(2)	72.0(2)	124.6(2)
O(222)	3.054(7)					78.1(2)	79.6(2)	90.9(2)
O(222^{vi})	2.903(7)						136.8(2)	73.9(2)
O(262^i)	2.946(7)							70.0(2)
O(262^{vii})	2.971(7)							

Transformations of the asymmetric unit: i $x-0.5, y, 0.5-z$ ii $0.5+x, y, 0.5-z$ iii $x+1, y, z$ iv $0.5+x, 0.5-y, 1-z$
v $x, 0.5-y, 0.5+z$ vi $1-x, \bar{y}, 1-z$ vii $0.5-x, y, 0.5+z$.

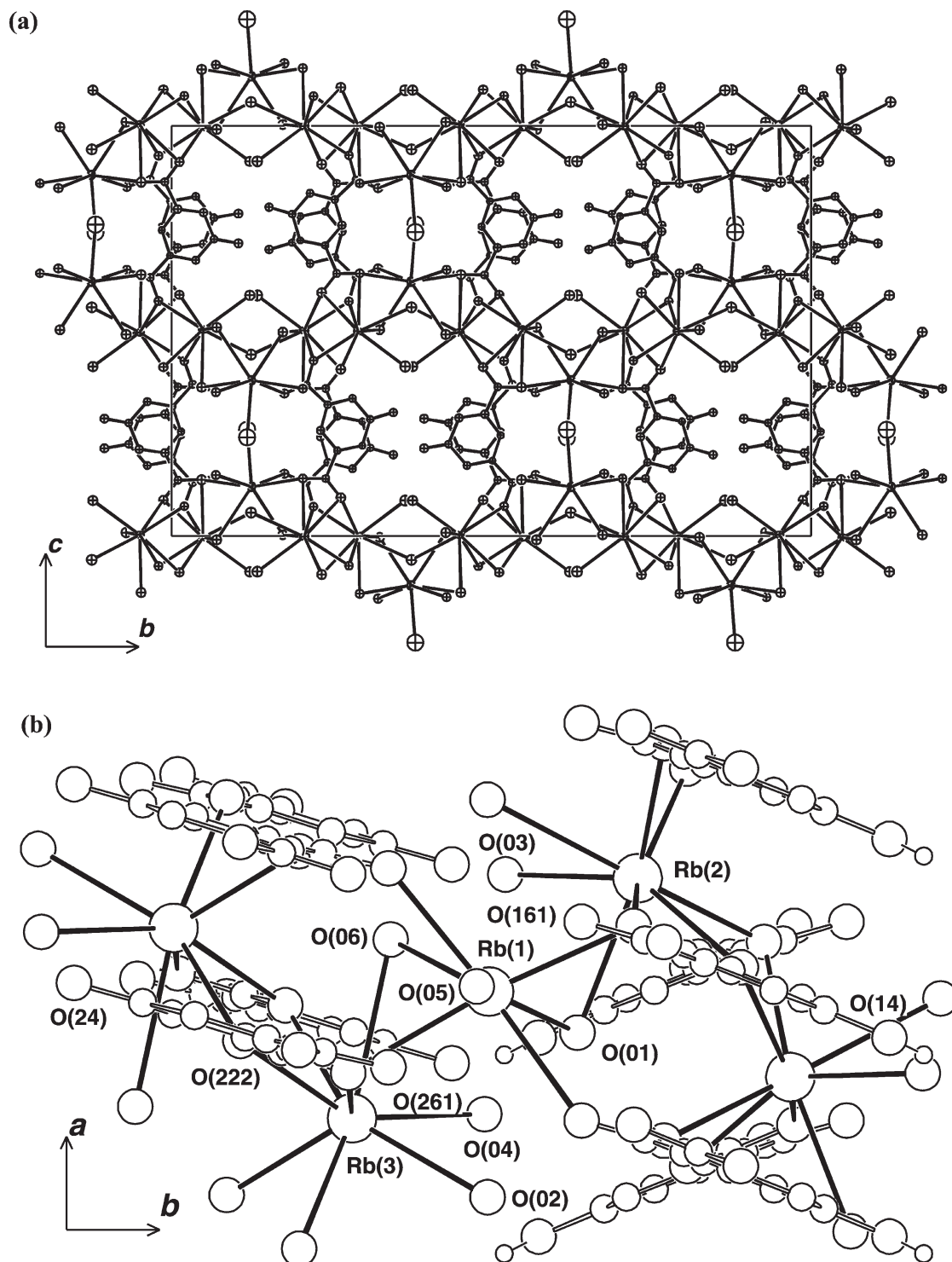S. BURNET *et al.*

(a)

(b)

FIGURE 9 (a) Unit cell contents of Rb$_3$(CHEL)(HCHEL)·6H$_2$O projected down *a*. (b) A segment of the cell contents projected down *c*.

coordination chemistry [43,47], their forms and the predominance of *O*-atom coordination are unsurprising, though in detail there is considerable variety. In all cases, the metal ions are constituents of polymeric arrays (described above), again unsurprising given the relatively low stoichiometric ratio of donor sites to metal atoms but interestingly

associated with a variety of polymerisation modes. Along with these variations attributable to the differing characteristics of the metal ions, however, there do appear to be persistent features of the lattices when a particular ligand is considered.

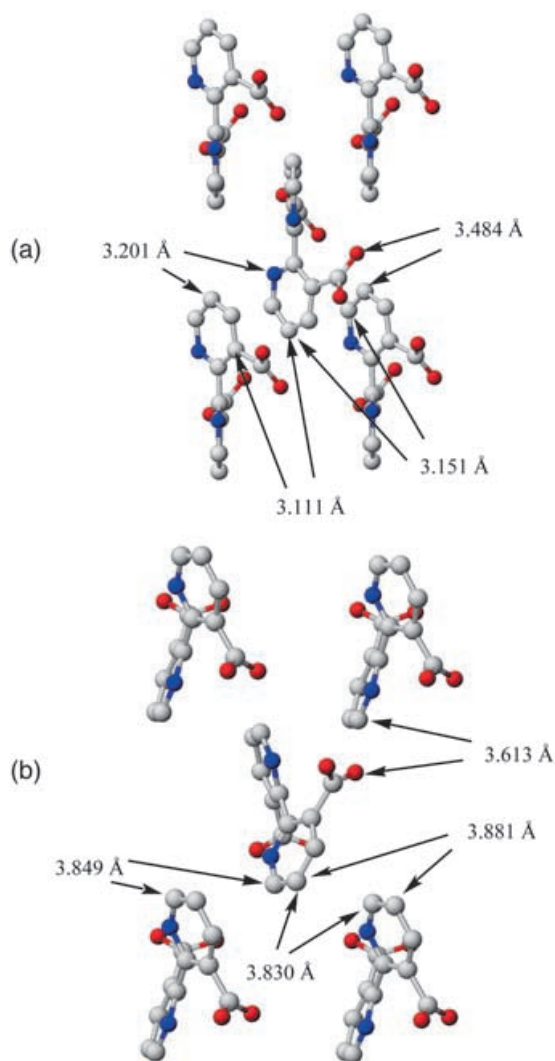In its complexes with Na, K, Rb and Cs, 2,2′-bipyridine-3,3′-dicarboxylate adopts a conformation

FIGURE 10 (a) Partial view of the lattice of K$_2$BDC·4H$_2$O, indicating the nature of the interdigitation which occurs between (horizontal in the page) columns of ligand entities and showing some of the closer interatomic distances. (b) A similar view of ligand interdigitation in the Cs$_2$BDC·4H$_2$O lattice, the closer interatomic contacts here being considerably longer.

latter are not obviously associated with the parallel arrays of aromatic units apparent in the lattice. The proton complex, somewhat like picric acid [5], involves close approaches of certain ring atoms to substituent atoms of another ring nearly orthogonally inclined to the first. C(5)···O(32) is 3.472(2) Å, and C(6)···O(32) 3.555(2) Å, while C(5)···C(3′) is 3.774(2) Å. In all the M$_2$BDC lattices, it is possible to discern some degree of interdigitation of columns of parallel aromatic units which may be indicative of limited π-stacking interactions, seemingly much more marked for the Na and K than the Rb and Cs complexes. Simplified views of the arrays present in the Na and Cs complexes are shown in Fig. 10. The arrays of overlapping rings seen in the Na and K compounds are similar to those seen in the dimethyl ester [48] and in the bis(N-oxide) [49] derivatives of the acid.

In the dilithium complex of chelidamate dianion, the lithium shows only tetrahedral O$_4$ coordination (Fig. 5) despite the presence of what may be considered as an amine-N donor in the pyridone form of the ligand. Exclusive O-coordination seems also to be the case in the Na and K compounds, as it is for their analogues derived from H$_2$BDC. In M$_2$BDC, M = Rb and particularly Cs, however, there is clear evidence for N-coordination, M–O and M–N distances being comparable, suggesting the pyridine-N donor of BDC^{2-} to be stronger as an alkali metal ion binder than the amine-N of chelidamate, as even in anhydrous Cs$_2$CHEL, the shortest Cs···N distance is 3.973(5) Å, considerably greater than any of the Cs–O distances taken as indicative of coordination.

CONCLUSIONS

In general, it is difficult to make clearcut assignments of the coordination numbers of the heavier alkali metal ions [5,19], presumably because there is no need for particularly strong interactions to stabilise the cations. This, unfortunately, does not justify the assumption that with the heavier alkali metal derivatives the structural influence of attractive inter-ligand forces may be more prominent, since there is still the (repulsive) factor of size to be allowed for. In any case, in the present chelidamate series, it is apparent that stacking of the planar ligand units occurs in all the lattices. Although the interplanar spacing is close to 3.5 Å in all, the pairwise projections of one ring on another vary considerably depending on the associated metal (Fig. 11), the Li system being unique in that adjacent rings have diametrically opposed orientations and in that there are two clearly different types of stacking projections. On the basis of atomic charges deduced by AM1 level calculations
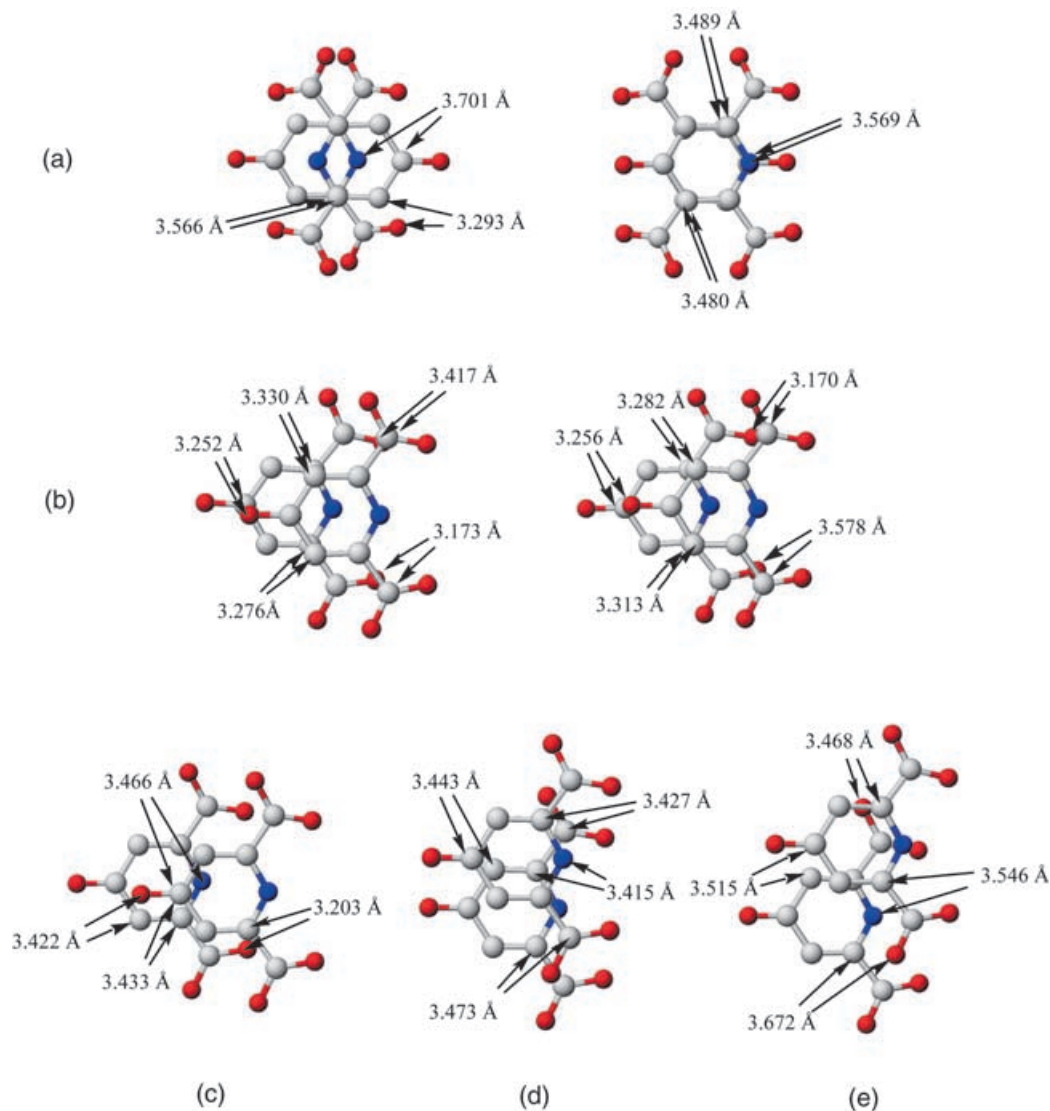
in which twisting of the biaryl unit, in the transoid rather than the cisoid sense, is approximately half that in the proton complex (acid), with the differences in dihedral angle within and between the isomorphous pairs (Na, 39.79(3), K, 48.93(6); Rb, 41.21(6), Cs, 41.62(6)°) being small for the Rb, Cs pair but surprisingly larger for the Na, K (Table II), perhaps a concomitant of the considerable (14 %) change in cell volume. An approach of one oxygen atom of each carboxylate to within <3 Å of the bridgehead carbon (as well as adjacent C and N atoms) of the linked aromatic ring is found in all systems, as in the proton complex. This may reflect some intramolecular "stacking" which is perhaps associated with significant intermolecular interactions, though at least in the proton complex the

FIGURE 11   Projections, perpendicular to the mean plane of the nearer chelidamate ring, of adjacent chelidamate rings found in the π-stacked columns present in the lattices of (a) $Li_2CHEL \cdot 4H_2O$. The different pairs alternate down the columns, giving rise to various interatomic contacts, some of the closer being shown. (b) $[Na_5CHEL(CHELH)_3(OH_2)_{10}] \cdot 28.6H_2O$-the very slight differences between adjacent pairs in the stacking column may be a reflection of differences in protonation of ligand entities. (c) $(NH_4)_2CHEL \cdot 4H_2O$. Here, as with the K and Cs complexes, the stacked columns appear to involve a single form of the projection of one ring on the next. Again, some of the closer atomic contacts are shown. (d) $K_8CHEL_4 \cdot 6H_2O$, with some closer contacts shown. (e) Cs_2CHEL, with some closer contacts shown.

for the pyridone form of chelidamic acid [50], all these projections are, however, consistent with close approaches involving a negative centre on one ligand unit and a positive centre on another, a model of π-stacking which has, of course, been applied in more complicated systems such as those involving porphyrins [51]. Thus, it appears that, at least in the case of chelidamates, π-stacking can be maintained while there is adaptation of the rest of the lattice to very different requirements of metal ion coordination. In these instances, it can therefore be argued that stacking interactions are a dominant determinant of the structure, while in complexes of bipyridine dicarboxylate, limitations on the degree of overlap of parallel molecular planes concomitant with the twisting of the biaryl unit may be associated with weaker stacking energies and hence explain the more varied ligand juxtapositioning seen in these compounds. Finally, this view of such systems as arrays of parallel planes which adapt largely by in-plane gliding and/or turning to accommodate other species such as cations and solvent, is given point by the 'unrelated' structure of the '*quasi*-isoelectronic' (to the chelidamate) system of unsolvated 2,6-diacetylpyridine (Table IV, Fig. 12), with a lattice array not unlike that of hydrated ammonium chelidamate!
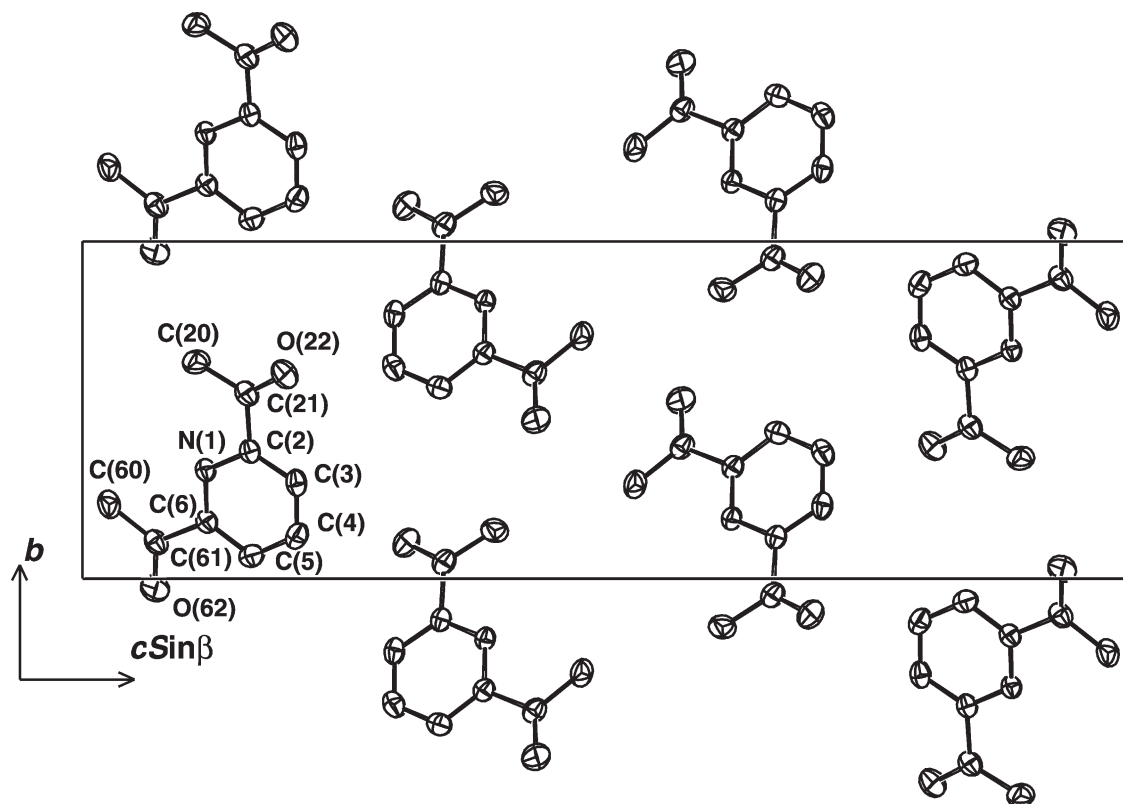
FIGURE 12   Unit cell contents of 2,6-diacetylpyridine projected down *a*.

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