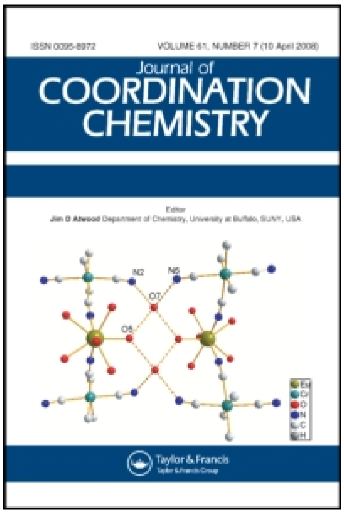

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Syntheses and crystal structures of rubidium and cesium 3,5-dinitropyrid-2-onate, 3,5-dinitropyrid-4-onate and 3,5-dinitro-4-pyridone-N-hydroxylate

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Six complexes, rubidium and cesium 3,5-dinitropyrid-2-onate (2DNPO), 3,5-dinitropyrid-4-onate (4NDPO), 3,5-dinitropyrid-4-one-N-hydroxylate (4DNPNO), were synthesized and characterized by elemental analysis, FT-IR, TG-DTG and X-ray single-crystal diffraction analysis. All the complexes crystallized from water and one of them was a hydrate. Rubidium 3,5-dinitropyrid-4-one-N-hydroxylate was crystallized with the 1 : 2 stoichiometry as $Rb[H(4DNPNO)_2]$ upon absorption of carbon dioxide. The structural determinations showed that the coordination sphere around a metal centre is made up of oxygen atoms and nitrogen atoms, except for the 4DNPNO complexes, where the coordination sphere accommodates exclusively oxygen atoms. The coordination numbers of the metal centers vary from 8, 10, 11 to 12, while the ligands, each employing its pyridone tautomer, link with metal cations. Bridging oxygen atoms play an important role in construction of two- and/or three-dimensional networks of these complexes. Hydrogen bonding contributes to the connectivity within a given sheet in $Rb[H(4DNPNO)_2]$; aromatic π–π stacking interactions exist only in Cs(4DNPNO). The interactions between metal atoms and ligands are generally very weak. The organization of all layer structures appears to be governed mainly by steric effects and electrostatic forces with very little directional influence of the cations. The thermogravimetric analyses of these complexes showed the following consecutive processes: loss of NO_2 groups, collapse of the pyridyl ring backbones and finally inorganic residue formation. These complexes could be used as probes in template effects of heavy alkali-metal cations in the organization of biorelevant ligands and as environment-friendly energetic catalysts in solid propellants.

Keywords: Rubidium compounds; Cesium compounds; 3,5-Dinitropyrid-2-onate; 3,5-Dinitropyrid-4-onate; 3,5-Dinitropyrid-4-one-N-hydroxylate

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1. Introduction

Interaction of common alkali-metal (Na^+, K^+) and alkaline-earth-metal (Mg^{2+}, Ca^{2+}) cations to biorelevant ligands is of great interest since these metals are abundant in biological systems [1]; shortages in food will cause deficiency syndromes [2]. Recent work has contributed considerably to a better understanding of the action of these cations on a molecular level, although many details remain unexplored [1–5]. By contrast, the role of the heavier alkali metals (Rb^+, Cs^+) and alkaline-earth (Sr^{2+}) have not received much attention, because these elements are relatively rare or even absent in biological systems and therefore are not considered essential, according to the current knowledge [6].

Our group focused on the chemistry of rubidium and cesium, involving interactions of Rb^+ and Cs^+ with human erythrocytes [7a], saccharides [7b] (D-glucose, D-fructose and D-sucrose) and α-amino acids [7c] (L-glycine, L-alanine and α-aminobutyric acid). We have also studied the coordination chemistry of Rb and Cs cations towards boric acid [8a, b], biorelevant ligands [8c] and energetic organic compounds [8d–g].

A variety of substituted dinitropyridone compounds are used as herbicidal chemicals or as important intermediates for oxidative dyestuffs, medicines and agrochemicals [9a, 9b]; some nitropyridone derivatives have nonlinear optic properties [9c]. Moreover, nitropyridone derivatives themselves and their metal complexes have higher explosion temperature and lower sensitivity and, therefore, are used as energetic catalysts for solid propellants in order to adjust and improve their trajectory properties [9d–f]. In general, a pyridone compound has two tautomerization forms: pyridone and hydroxylpyridine. An investigation of the molecular structures of metal complexes derived from pyridone compounds will help to understand which form coordinates with metal atoms. In order to get insight into coordination modes of heavy alkali and alkaline-earth metal cations towards dinitropyridone compounds and look for environment-friendly energetic catalysts, we have recently synthesized a number of alkali and alkaline-earth metal compounds derived from *ortho* or *para* 3,5-dinitropyridone (–N-hydroxide) ligands. In the present article, the preparations, molecular structures and thermal analyses of six Rb(I) and Cs(I) compounds of 3,5-dinitropyrid-2-onate (2DNPO), 3,5-dinitropyrid-4-onate (4DNPO), 3,5-dinitro-4-pyridone-N-hydroxylate (4DNPNO) are reported.

2. Experiment

2.1. *Preparations*

All complexes were readily prepared by neutralization of a dinitropyridone compound with the corresponding alkali hydroxides in aqueous solution. The products are highly soluble in water, so single-crystal growth was only successful under empirically modified conditions in each case. Only cesium 3,5-dinitropyrid-2-onate was obtained as a hydrate, others as anhydrous compounds (scheme 1). All of the reactants were added with the same 1 : 1 stoichiometry; rubidium 3,5-dinitro-4-pyridone-N-hydroxylate, however, crystallized with 1 : 2 stoichiometry as $Rb[H(4DNPNO)_2]$, possibly due to adsorption of carbon dioxide in air during the preparation and single-crystal growth forming rubidium bicarbonate (scheme 2), as observed in the crystallization of

$$\mathrm{CsOH + H(2DNPO)} \xrightarrow{\mathrm{H_2O}} \mathrm{Cs(2DNPO)(H_2O)}$$

Scheme 1. The synthetic route of Cs (2DNPO)(H_2O).

$$\mathrm{2RbOH + 2H(4DNPNO) + CO_2} \xrightarrow[\text{in air}]{\mathrm{H_2O}} \mathrm{Rb[H(4DNPNO)_2] + H_2O + RbH\ CO_3}$$

Scheme 2. The synthetic route of Rb[H(4DNPNO)$_2$].

Cs[H(Anth]$_2$] under atmospheric conditions [6b]. All products are stable in air and not hygroscopic. The Cs(2DNPO)(H_2O) readily loses water when exposed to a vacuum.

2.2. *Synthesis*

The procedure to synthesize the six complexes is the same and, therefore, we only describe the synthesis of one complex as an example.

2.2.1. Rubidium 3,5-dinitropyrid-2-onate (I Rb(2DNPO)). Rubidium hydroxide (1.02 g, 10 mmol) was added to a suspension of 3,5-dinitropyrid-2-one (1.85 g, 10 mmol) in 20 mL of water. Then the suspension was heated to 60°C under stirring and kept at this temperature for 30 min. The solution was concentrated to 5 mL by vacuum and set aside for crystallization. Yellow crystals suitable for single-crystal X-ray diffraction analysis were obtained by slow evaporation of the complex in water at room temperature after several weeks. Yield: 0.43 g (16.0%). Elemental analysis Calcd for Rb(2DNPO) ($C_5H_2N_3O_5Rb$): C 22.28, H 0.75, N 15.59, Rb 31.71; Found: C 21.46, H 0.82, N 15.71, Rb 31.85%. IR (KBr, cm^{-1}): 1617, s, ν_{asym}(C=O); 1582, s, ν_{sym}(C=O); 1532, s, ν_{asym}(N–O); 1467, m, ν(C–N); 1428, s, ν(C=C); 1326, s, ν_{sym}(N–O); 1269, s, δ(=C–H); 1105, m, δ(=C–H); 796, m, γ(=C–H).

2.2.2. Cesium 3,5-dinitropyrid-2-onate monohydrate(II Cs(2DNPO)(H_2O)). Yield: 0.73 g (21.8%). Elemental analysis Calcd for Cs(2DNPO)(H_2O) ($C_5H_4N_3O_6Cs$): C 17.93, H 1.20, N 12.54, Cs 39.67; Found: C 17.29, H 1.00, N 12.71, Cs 39.84%. IR (KBr, cm^{-1}): 3398, m(br), ν(O–H); 3087, m, ν(=C–H); 1622, s, ν_{asym}(C=O); 1532, s, ν_{asym}(N–O); 1467, m, ν(C–N); 1429, s, ν(C=C); 1336, s, ν_{sym}(N–O); 1271, s, δ(=C–H); 1105, m, δ(=C–H); 796, m, γ(=C–H); 700, m, γ(O–H).

2.2.3. Rubidium 3,5-dinitropyrid-4-onate (III Rb(4DNPO)). Yield: 0.52 g (19.3%). Elemental analysis Calcd for Rb(4DNPO)($C_5H_2N_3O_5Rb$): C 22.28, H 0.75, N 15.59, Rb 31.71; Found: C 22.66, H 0.61, N 15.59, Rb 31.59%. IR (KBr, cm^{-1}): 1675, s, ν_{asym}(C=O); 1541, s, ν_{asym}(N–O); 1485, m, ν(C–N); 1408, s, ν(C=C); 1350, s, ν_{sym}(N–O); 1269, s, ν_{sym}(N–O); 1119, m, δ(=C–H); 796, s, γ(=C–H).

2.2.4. Cesium 3,5-dinitropyridin-4-onate(IV Cs(4DNPO)). Yield: 0.71 g (22.4%). Elemental analysis Calcd for Cs(4DNPO)($C_5H_2N_3O_5Cs$): C 18.94, H 0.64, N 13.26, Cs 41.93; Found: C 19.44, H 0.75, N 12.91, Cs 42.27%. IR (KBr, cm^{-1}): 1649, s, ν_{asym}(C=O); 1511, s, ν_{asym}(N–O); 1470, s, ν(C=N); 1420, s, ν(C=C); 1356, s, ν_{sym}(N–O); 1283, s, ν_{sym}(N–O); 1179, m, δ(=C–H); 782, s, γ(=C–H).

2.2.5. Rubidium hydrogen *bis*(3,5-dinitro-4-pyridone-N-hydroxylate) (V Rb[H(4DNPNO)$_2$]). Brown crystals were collected, 0.46 g (9.5%). Elemental analysis Calcd for Rb[H(4DNPNO)$_2$] ($C_{10}H_5N_6O_{12}Rb$): C 24.68, H 1.04, N 17.27, Rb 17.56; Found: C 22.98, H 1.06, N 17.04, Rb 17.16%. IR (KBr, cm^{-1}): 3425, m(br), ν(O–H); 1675, s, ν_{asym}(C=O); 1541, s, ν_{asym}(N–O); 1506, m, ν(C=N); 1485, s, ν(C=C); 1350 s, ν_{sym}(N–O); 1277, s, ν_{sym}(N–O); 1119, m, δ(=C–H); 799, s, γ(=C–H).

2.2.6. Cesium 3,5-dinitro-4-pyridone-N-hydroxylate(VI Cs(4DNPNO)). Brown crystals were collected, 0.61 g (18.4%). Elemental analysis Calcd for Cs(4DNPNO) ($C_5H_2N_3O_6Cs$): C 18.03, H 0.61, N 12.62, Cs 39.91; Found: C 16.65, H 0.55, N 13.01, Cs 40.18%. IR (KBr, cm^{-1}): 1660, s, ν_{asym}(C=O); 1574, s, ν_{asym}(N–O); 1495, m, ν(C=N); 1453, m, ν(C=C); 1342, s, ν_{sym}(N–O); 1233, s, ν_{sym}(N–O); 1143, m, δ(=C–H); 794, s, γ(=C–H).

2.3. *Physical measurements*

3,5-Dinitropyrid-2-one, 3,5-dinitropyrid-4-one and 3,5-dinitro-4-pyridone-N-hydroxide were synthesized following methods previously described with slight modifications [9e, 10]. RbOH and CsOH were of analytical reagent grade and used directly without further purification. All experiments were carried out in twice distilled water. The infrared spectra were recorded as KBr pellets on a Nicolet 170SX FT-IR spectrometer. The crystal structures were determined with a Bruker Smart-1000 CCD diffractometer. Elemental analyses (C, H, N) were determined with a German Vario EL III instrument. The DCS and TG-DTG measurements were done with a Thermoanalyzer Systems Q1000DSC + LNCS + FACS Q600SDT of TA company.

2.4. *Single crystal X-ray diffraction analysis*

The determination of the unit cell and the data collection for the complexes **I** to **VI** were performed on a Bruker Smart-1000 CCD diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) using the $\omega - 2\theta$ scan technique. The structures were solved by direct methods using SHELXS-97 [11] and refined against F^2 by full matrix least-squares using SHELXL-97 [12]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were treated using a riding model. The crystals used for the diffraction study showed no decomposition during data collection. A summary of the crystal data, experimental details and refinement results are listed in table 1.

Table 1. Crystallographic data for **I** to **VI**.

	I	**II**	**III**	**IV**	**V**	**VI**
Chemical formula	$C_5H_2N_3O_5$ Rb	$C_{20}H_{16}Cs_4$ $N_{12}O_{24}$	$C_{10}H_4N_6O_{10}Rb_2$	$C_5H_2CsN_3$ O_5	$C_{10}H_5N_6O_{12}Rb$	$C_5H_2CsN_3$ O_6
M_r	269.57	1340.09	539.13	317.01	486.67	333.01
Crystal symmetry	Triclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2(1)/n$	$P2(1)/c$	$P2(1)/c$	$P\bar{1}$	$C2/c$
a (Å)	4.225(11)	4.7828(6)	4.0208(6)	4.1555(5)	8.0456(2)	18.921(15)
b (Å)	9.025(2)	20.297(3)	14.651(2)	14.912(17)	9.6263(3)	7.7396(6)
c (Å)	10.839(3)	9.4790(13)	13.6397(19)	13.9319(16)	10.5238(3)	15.2842(11)
α (°)	91.983(4)	90	90	90	87.392(2)	90
β (°)	90.621(4)	95.573(10)	92.991(2)	94.262(10)	89.515(2)	126.89(10)
γ (°)	103.047(4)	90	90	90	79.156(2)	90
V (Å^3)	402.31(18)	915.8(2)	802.4(2)	860.93(17)	799.68(4)	1790.1(2)
Z	2	4	4	4	2	8
Reflections collected	1968	5928	6780	7298	7419	5243
Independent reflections	1333	2014	1836	1982	3615	2048
R_1, wR_2 indices	0.0450, 0.1195	0.0173, 0.0358	0.0370, 0.0624	0.0235, 0.0588	0.0668, 0.1453	0.0330, 0.0743
$I>2\sigma(I)$	0.0511, 0.1232	0.0156, 0.0351	0.0258, 0.0582	0.0210, 0.0572	0.0485, 0.1324	0.0248, 0.0696

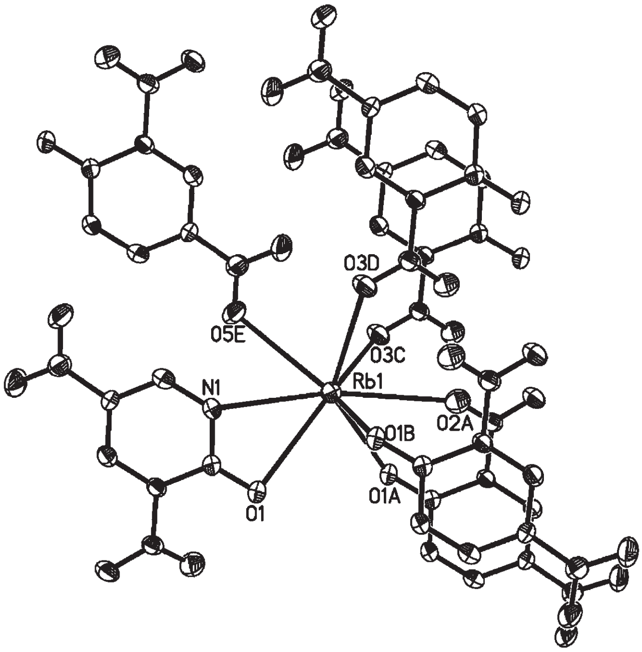

Figure 1. Eight-coordinate rubidium cation of **I** (30% ellipsoids).

3. Results and discussion

3.1. *Rb(2DNPO) I*

Compound **I** is anhydrous and crystallizes in the triclinic space group $P\bar{1}$, with two formula units in the unit cell. The asymmetric unit contains one rubidium cation and one 3,5-dinitropyrid-2-one anion. Each rubidium atom is eight-coordinate with six ligands, of which two are η^2-chelate-ligands and four η^1-chelate-ligands. The two η^2-chelate-ligands are linked to the rubidium cation with different donor atoms, namely, η^2 ($O_{carbonyl}$ and O_{NO_2}) and η^2 ($O_{carbonyl}$ and N_{py}); the four η^1-chelate-ligands coordinate to the metal center with three O_{NO_2} and one $O_{carbonyl}$. (Figure 1) The Rb–N distance is long (3.113(5) Å); the Rb–O contacts range from 2.895(4) Å (for O1A) to 3.216(5) Å (for O5E). The C1–O1 bond distance is 1.233(6) Å, longer by 0.1 Å than that in the free ligand (1.223(3) Å) [10a], consistent with the IR peak at 1617 cm^{-1} (stretching of CO group of the 2-pyridonate) shifting ca 73 cm^{-1} wavenumbers upon coordination with rubidium. These two aspects indicate the weakening of the carbonyl bond strength after coordination. Upon comparison with normal C–O single bond (1.30–1.39 Å) [10d], the C1–O1 distance is much shorter, indicating that the ligand adopts its pyridone tautomer upon coordination (table 2). Figure 2 shows the coordination of the ligand with six rubidium cations. There are two different kinds of bridging oxygen atoms, O1(from the carbonyl group) and O3 (from one of two nitro groups). The O1 atom acts as a bridge of three rubidium cations, forming a tetrahedral configuration. The O3 bridges connect the rubidium cations along the *a*-axis. Two kinds of bridges assemble the groups along the *a*-axis as an infinite strengthened ladder.

Table 2. Selected bond lengths (Å) and angles (°) of **I**.

Rb(1)–O(1A)	2.895(4)	Rb(1)–O(2A)	3.042(5)
Rb(1)–O(1B)	2.936(4)	Rb(1)–N(1)	3.113(5)
Rb(1)–O(3D)	2.945(5)	Rb(1)–O(3C)	3.133(4)
Rb(1)–O(1)	3.022(4)	Rb(1)–O(5E)	3.216(5)
O(1)–C(1)	1.233(6)		
O(1)–Rb(1)–O(2A)	122.60(12)	O(1)–Rb(1)–O(3C)	124.70(11)
O(1)–Rb(1)–N(1)	43.18(11)	O(1)–Rb(1)–O(5E)	97.63(12)

Symmetry code: A = $(-x+1, -y+2, -z+1)$, B = $(-x+2, -y+2, -z+1)$, C = $(x+1, y+1, z)$, D = $(x, y+1, z)$, E = $(-x+2, -y+2, -z+2)$.

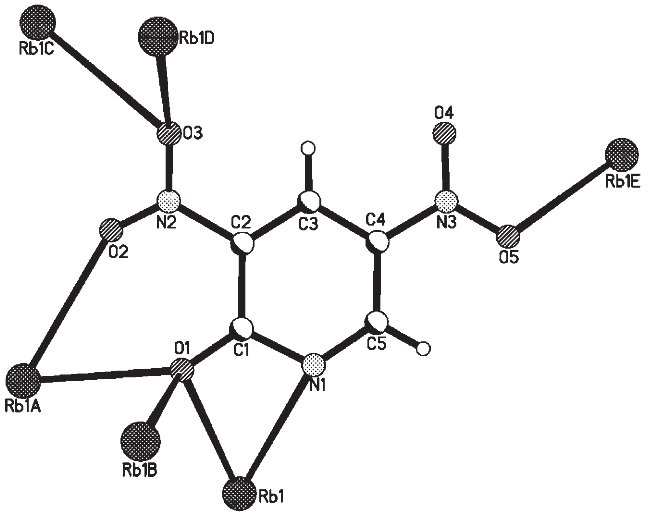

Figure 2. Binding modes of 3,5-dinitropyrid-2-one anion towards rubidium in **I**.

3.2. *Cs(2DNPO)(H_2O) II*

Cs(2DNPO)(H_2O) crystallizes in the monoclinic space group $P2(1)/n$ with four formula units in the unit cell. The asymmetric unit contains four cesium cations, four 3,5-dinitropyrid-2-one anions and four water molecules. The inner coordination sphere accommodates twelve atoms (figure 3). The Cs–O distances cover a wide range from 3.1235(18) Å (for O1) to 3.5636(19) Å (O1A is excessively long and should be considered a borderline case); the Cs–N3F distance (3.7327(18) Å) is also extremely long, meaning the Cs–N interaction is very weak, not comparable in strength to the Cs–N interactions in compound **V** (see table 3 and table 7). The C1–O2 bond distance is 1.243(3) Å, considerably longer than in the free ligand (1.223(3) Å) [10a]. The coordination sphere of cesium is completed by three water molecules, which are all in bridging positions to three neighboring metal atoms. The water molecule (H1W/O1/H2W) is also engaged in hydrogen bonding with O2, N3A $(x+1/2, -y+3/2, z+1/2)$ of two ligands (table 4).

Cs(2DNPO)(H_2O) is unique containing coordinated water in rare triply-bridging positions [6b] between cesium cations with distances varying from 3.1235(18) Å to 3.5636(19) Å (table 3). The interactions among cations, anions, and water dipoles in the lattice of Cs(2DNPO)(H_2O) are largely undirectional and determined by steric effects

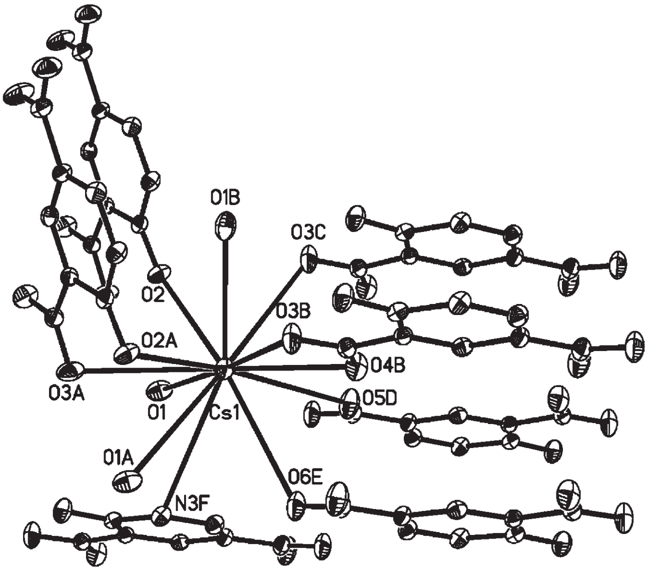

Figure 3. 12-Coordinate cesium of **II** (30% ellipsoids).

Table 3. Selected bond lengths (Å) and angles (°) of **II**.

Cs(1)–O(1)	3.1235(18)	Cs(1)–O(3C)	3.360(2)
Cs(1)–O(5D)	3.1590(17)	Cs(1)–O(3A)	3.3838(19)
Cs(1)–O(2)	3.2368(15)	Cs(1)–O(3B)	3.5187(18)
Cs1–O(2A)	3.2455(17)	Cs(1)–O(6E)	3.5378(19)
Cs(1)–O(4B)	3.2789(16)	Cs(1)–O(1A)	3.5636(19)
Cs(1)–O(1C)	3.282(2)	Cs(1)–N(3F)	3.7327(18)
O(2)–C(1)	1.243(3)		
O(1)–Cs(1)–O(5F)	94.67(5)	O(1)–Cs(1)–O(3C)	95.28(5)
O(1)–Cs(1)–O(2)	52.55(4)	O(1)–Cs(1)–O(1A)	91.08(5)
O(1)–Cs(1)–O(2A)	112.13(5)	O(1)–Cs(1)–O(6E)	111.81(4)
O(1)–Cs(1)–O(4B)	149.29(5)	O(1)–Cs(1)–O(3B)	174.08(5)
O(1)–Cs(1)–O(1C)	117.19(4)	O(1)–Cs(1)–O(3A)	64.10(5)

Symmetry code: A = ($x-1$, y, z), B = ($-x+1$, $-y+1$, $-z$), C = ($-x+2$, $-y+1$, $-z$), D = ($-x+1$, $y-1/2$, $-z-1/2$), E = ($x-1$, $-y+3/2$, $z-1/2$), F = (x, $-y+3/2$, $z-1/2$).

Table 4. Hydrogen bond lengths (Å) and angles (°) in **II**.

D–H···A	d(D–H)	d(H···A)	d(D···A)	D–H···A
O(1)–H(2W)···N(3A)	0.825(18)	2.090(18)	2.912(2)	175(4)
O(1)–H(1W)···O(2)	0.823(16)	2.11(2)	2.817(2)	144(3)

Symmetry code: A = $x+1/2$, $-y+3/2$, $z+1/2$.

and Coulomb forces [6b]. Together with the cesium cations, the polar groups of the ligands form an inner layer of a sandwich, which is covered on both sides by the aromatic rings (figure 4). These sandwich layers stack with long van der Waals contacts between the pyridyl-ring covers.

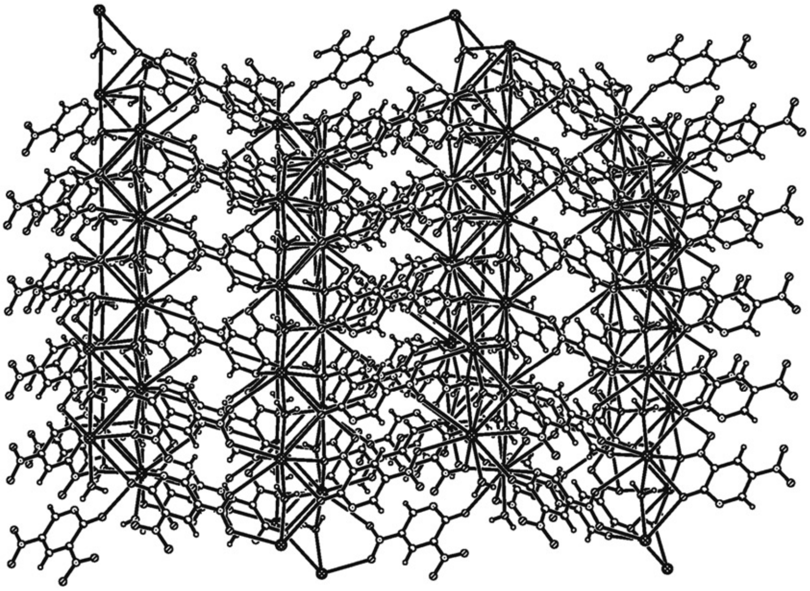

Figure 4. Formation of layers in **II**. The inner domains formed of the cesium ions. The water molecules are shielded by aromatic rings.

3.3. *Rb(4DNPO) III and Cs(4DNPO) IV*

Both complexes are very similar and will be described together. Crystals of both Rb(4DNPO) and Cs(4DNPO) are monoclinic with space group *P*2(1)/*c*. The coordination environments of the cations and the anions are same, too. Both asymmetric units comprise two rubidium (or cesium) cations and two 3,5-dinitropyrid-4-one anions. Each cation is ten-coordinate with three *O*,*O*-chelating, two *O*-monodentate and two *N*-monodentate ligands (one metal center as the reference); one 3,5-dinitropyrid-4-one anion coordinates seven rubidium ions (figure 5). The Rb–O distances span a range from 2.8206(18) Å for O3C to 3.601(3) Å for O4C, but the Rb–N contacts are in the narrow range from 3.121(2) Å for N1E to 3.204(2) Å for N1F (table 5). Meanwhile, the Cs–O distances cover a range from 2.958(2) Å for O1A to 3.700(3) Å for O4, with Cs–N in the narrow range (3.237(3) Å for N1E and 3.320(3) Å for N1F) (table 6). The O(3)–C(3) distances (1.245(3) Å in **III** and 1.243(3) Å) in **IV**) are slightly longer than typical C=O distances [10b].

Both Rb(4DNPO) and Cs(4DNPO) contain oxygen bridges linking to the cations in the crystals (figure 6 shows **III** as an example). The individual fragments along the *c*-axis assemble in a parallelogram structure of a planar four-member ring containing two metal atoms and two bridging oxygen atoms forming M_2O_2, with the Rb $\cdots$ Rb distance of 5.760 Å and the Cs $\cdots$ Cs distance of 5.861 Å. Along the *a*-axis the metal ions are connected by two oxygen bridges and one nitrogen bridge in an infinite chain, with the Rb $\cdots$ Rb distance of 4.021 Å and the Cs $\cdots$ Cs distance of 4.156 Å. π–π-stacking of aromatic rings can be ruled out owing to the extremely long distances ($d > 4$ Å).

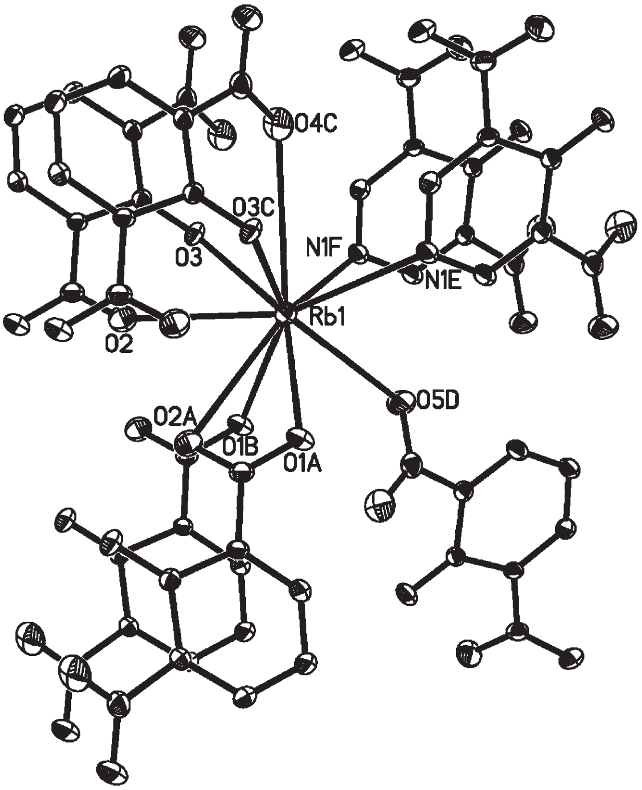

Figure 5. Ten-coordinate rubidium of **III** (30% ellipsoids).

Table 5. Selected bond lengths (Å) and angles (°) of **III**.

Rb(1)–O(3C)	2.8206(18)	Rb(1)–O(2)	3.105(2)
Rb(1)–O(3)	2.8351(19)	Rb(1)–N(1E)	3.121(2)
Rb(1)–O(1B)	2.971(2)	Rb(1)–N(1F)	3.204(2)
Rb(1)–O(5D)	3.071(2)	Rb(1)–O(2A)	3.337(2)
Rb(1)–O(1A)	3.091(2)	Rb(1)–O(4C)	3.601(3)
O(3)–C(3)	1.245(3)		
O(3)–Rb(1)–O(1B)	83.93(6)	O(3)–Rb(1)–N(1E)	123.39(6)
O(3)–Rb(1)–O(5D)	125.09(7)	O(3)–Rb(1)–N(1F)	69.00(5)
O(3)–Rb(1)–O(1A)	145.64(5)	O(3)–Rb(1)–O(2A)	107.23(5)
O(3)–Rb(1)–O(2)	55.74(5)	O(3)–Rb(1)–O(4C)	60.84(6)

Symmetry code: A = $(-x, -y, -z+1)$, B = $(-x+1, -y, -z+1)$, C = $(x-1, y, z)$, D = $(-x+1, y-1/2, -z+3/2)$, E = $(x-1, -y+1/2, z+1/2)$, F = $(x, -y+1/2, z+1/2)$.

3.4. *Rb[H(4DNPNO)$_2$] V*

Complex **V** crystallizes in the triclinic space group $P\bar{1}$ with $Z = 2$. The asymmetric unit contains one rubidium cation, one 3,5-dinitro-4-pyridone-N-hydroxide and one anion of it. The rubidium cations are 11-coordinate with seven ligands, three of which are neutral and the others anions (figure 7). There exist different coordination patterns: three of the four anion ligands adopt η^2 coordination mode through oxygen atoms of

Table 6. Selected bond lengths (Å) and angles (°) of **IV**.

Cs(1)–O(1A)	2.958(2)	Cs(1)–O(2C)	3.209(3)
Cs(1)–O(1)	2.960(2)	Cs(1)–N(1F)	3.237(3)
Cs(1)–O(2B)	3.121(3)	Cs(1)–N(1E)	3.320(3)
Cs(1)–O(5D)	3.188(3)	Cs(1)–O(3C)	3.449(3)
Cs(1)–O(3A)	3.196(3)	Cs(1)–O(4)	3.700(3)
O(1)–Cs(1)–O(2B)	144.29(7)	O(1)–Cs(1)–N(1F)	70.17(7)
O(1)–Cs(1)–O(5D)	139.43(9)	O(1)–Cs(1)–N(1E)	123.27(7)
O(1)–Cs(1)–O(3A)	74.10(8)	O(1)–Cs(1)–O(3C)	85.70(8)
O(1)–Cs(1)–O(2C)	83.11(7)	O(1)–Cs(1)–O(4)	47.06(6)

Symmetry code: A = $(x-1, y, z)$, B = $(-x+1, -y+1, -z)$, C = $(-x+2, -y+1, -z)$, D = $(-x+1, y-1/2, -z-1/2)$, E = $(x-1, -y+3/2, z-1/2)$, F = $(x, -y+3/2, z-1/2)$.

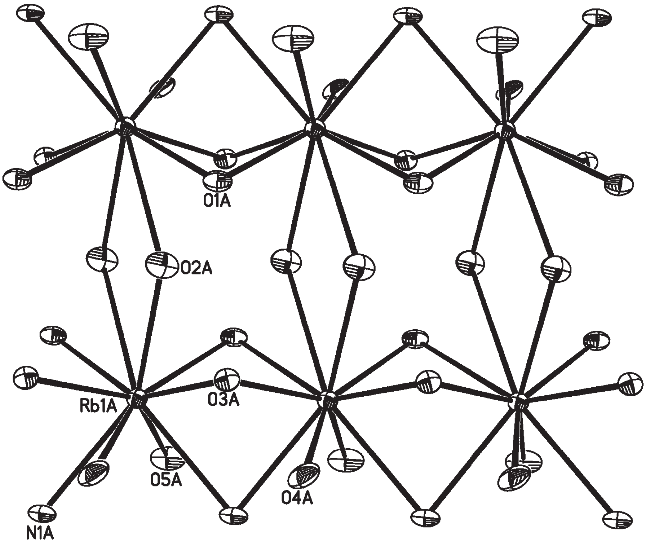

Figure 6. The extended array of complex **III** formed by two kinds of oxygen bridges coordinated to the cations in the crystal. Only the oxygen atoms linked with cations are shown for clarity.

nitro groups and carbonyl groups, while the fourth ligand links the metal atom by the N-hydroxide oxygen atom on the pyridine ring with η^1 mode; one of the three neutral ligands is bidentate with η^2 mode through oxygen atoms of one nitro group, while the other two link to the metal center by η^1 mode through a nitro oxygen atom. The Rb–O distances cover a wide range from 2.744(3) Å for O1 to 3.387(10) Å for O2 (table 7). The O7–C8 and N5–O10 distances are 1.215(5) and 1.359(4) Å, respectively, considerably shorter than those corresponding distances in free ligand (O–C = 1.251(8) and N–O = 1.393(8) Å) [10b].

In assembling the crystal structure, the rubidium cation links the neutral ligand and the anion ligand together. In a neutral ligand, the proton transfers from O1 to O4 (figure 8). A pair of 3,5-dinitro-4-pyridone-N-hydroxide anions is joined by a hydrogen bond involving the proton to form a homoconjugated anion, featuring the short and asymmetric hydrogen bond with the O–O distance equal to 2.435(3) Å. The asymmetric structure is expanded to a sheet by normal hydrogen bonds of the other hydrogen atoms

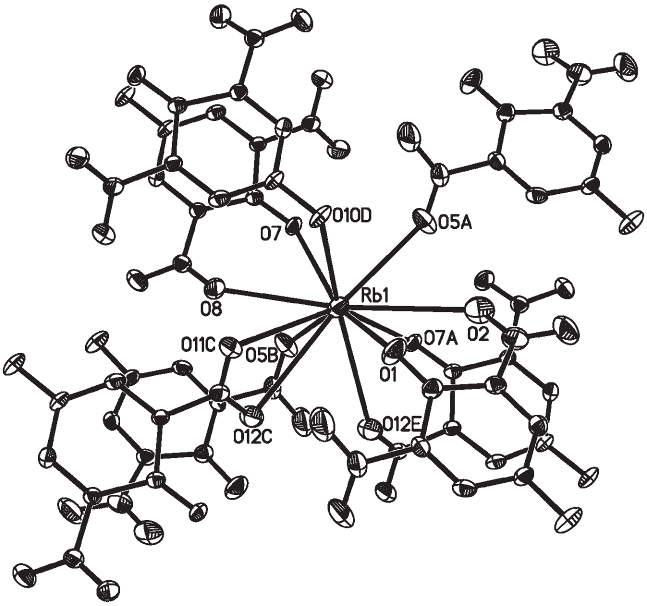

Figure 7. 11-Coordinate rubidium cation of **V** (30% ellipsoids).

Table 7. Selected bond lengths (Å) and angles (°) of **V**.

Rb(1)–O(1)	2.744(3)	Rb(1)–O(5A)	3.088(4)
Rb(1)–O(10D)	2.824(3)	Rb(1)–O(11C)	3.253(3)
Rb(1)–O(7)	2.881(3)	Rb(1)–O(12C)	3.327(3)
Rb(1)–O(7E)	2.933(3)	Rb(1)–O(5B)	3.363(5)
Rb(1)–O(8)	3.046(3)	Rb(1)–O(2)	3.387(10)
Rb(1)–O(12E)	3.049(4)	O(7)–C(8)	1.215(5)
O(10)–N(5)	1.359(4)		
O(1)–Rb(1)–O(10D)	77.75(10)	O(1)–Rb(1)–O(5A)	99.39(13)
O(1)–Rb(1)–O(7)	156.93(12)	O(1)–Rb(1)–O(11C)	75.95(10)
O(1)–Rb(1)–O(7E)	99.75(10)	O(1)–Rb(1)–O(12C)	81.08(12)
O(1)–Rb(1)–O(8)	129.69(11)	O(1)–Rb(1)–O(5B)	141.81(12)
O(1)–Rb(1)–O(12E)	68.42(13)	O(1)–Rb(1)–O(2)	50.22(17)

Symmetry code: A = $(x+1, y, z)$, B = $(-x+1, -y+1, -z+1)$, C = $(x-1, y, z)$, D = $(-x+2, -y+2, -z+1)$, E = $(-x+2, -y+1, -z+1)$.

in the homoconjugated anion (table 8). Above and below the layers neighboring pyridyl rings are at distances which rule out any significant contributions from π–π-stacking.

3.5. *Cs(4DNPNO) VI*

Cesium 3,5-dinitro-4-pyridone-N-hydroxylate, Cs(4DNPNO), crystallizes in the monoclinic space group, $C2/c$ with $Z = 8$. The asymmetric unit contains one cesium cation and one 3,5-dinitro-4-pyridone-N-hydroxide anion. Each cesium cation has contacts to seven anions with coordination number ten (figure 9). The Cs–O distances range from

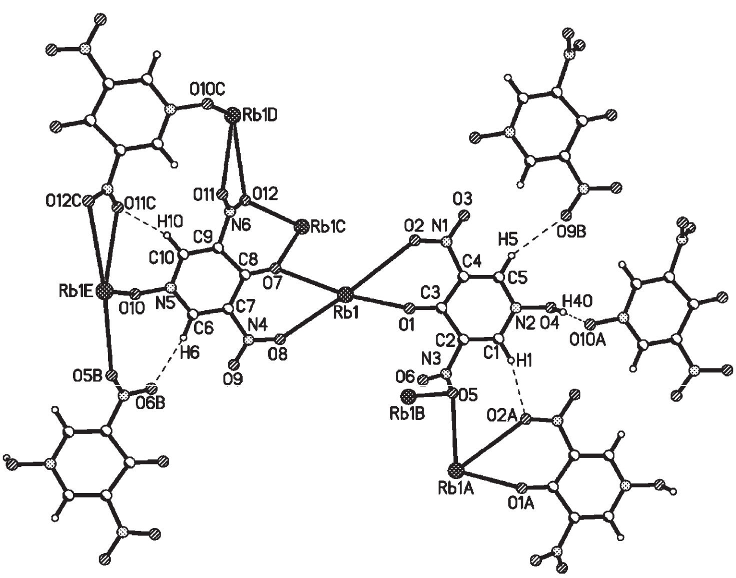

Figure 8. Coordination modes of the 3,5-dinitro-4-pyridone-N-hydroxide anion and its neutral form toward rubidium cations in **V**. Hydrogen bonds are shown by dashed lines.

Table 8. Hydrogen bond lengths (Å) and angles (°) for **V**.

D–H···A	d(D–H)	d(H···A)	d(D···A)	D–H···A
O(4)–H(4O)···O(10A)	0.84	1.60	2.4350	172
C(1)–H(1)···O(2B)	0.95	2.42	3.3355	163
C(5)–H(5)···O(9C)	0.95	2.56	3.4281	153
C(6)–H(6)······O(6D)	0.95	2.52	3.3417	145
C(10)–H(10)···O(11E)	0.95	2.54	3.3807	148

Symmetry code: A = 1 − *x*, 1 − *y*, −*z*, B = 1 + *x*, *y*, *z*, C = *x*, 1 + *y*, −1 + *z*, D = −1 + *x*, *y*, *z*, E = 1 − *x*, 1 − *y*, 1 − *z*.

3.048(2) Å for O6E to 3.680(3) Å for O4C (table 9); O3–C3 and N3–O6 distances are 1.243(3) and 1.336(3) Å, respectively, considerably shorter than those corresponding distances in free ligand (O–C = 1.251(8) and N–O = 1.393(8) Å) [10b]. One π–π-stacking interaction exists in this compound with the pyridyl ring (N3/C1–C5) contacting with the invertible ring (N3F/C1F–C5F) at a distance of Cg*–Cg# = 3.529 Å. One ligand anion is coordinated to seven metal cations (figure 10). The carbonyl oxygen atom bridges two metal atoms; one nitro group adopts μ_2-η^1: η^1 mode with cesium cations and another nitro group is linked to metal atoms in a μ_2-η^1: η^2 mode, while the pyridine-N-hydroxide anion bridges two cesium cations.

The versatile oxygen bridges have important roles; along the *b*-axis, the two-oxygen bridges and the four-oxygen bridges appear alternatively between adjacent cesium cations resulting in a corrugated chain (figure 11). Contrary to our expectation, the four-oxygen-atom bridged Cs–Cs distance (4.295 Å) is considerably longer than the two-oxygen-atom bridged Cs–Cs distance (4.135 Å). These abnormal Cs–Cs distances are probable due to steric effects. The corrugated chains are extended to a sheet by

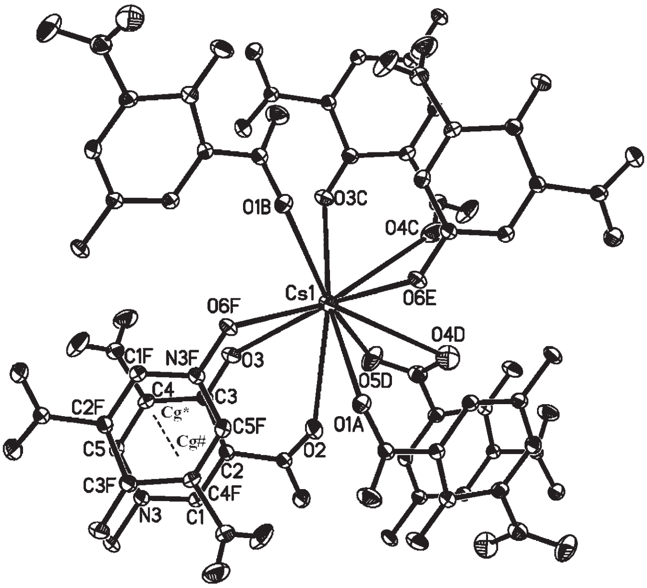

Figure 9. Ten-coordinate cesium cation of **VI** with intermolecular π–π-stacking interaction (30% ellipsoids).

Table 9. Selected bond lengths (Å) and angles (°) of **VI**.

Cs(1)–O(6E)	3.048(2)	Cs(1)–O(1B)	3.216(2)
Cs(1)–O(3)	3.070(2)	Cs(1)–O(4C)	3.269(3)
Cs(1)–O(3C)	3.070(2)	Cs(1)–O(5D)	3.308(3)
Cs(1)–O(6F)	3.162(2)	Cs(1)–O(1A)	3.321(2)
Cs(1)–O(2)	3.178(3)	Cs(1)–O(4D)	3.680(3)
O(3)–C(3)	1.243(3)	O(6)–N(3)	1.336(3)
O(3)–Cs(1)–O(3C)	95.33(5)	O(3)–Cs(1)–O(4C)	134.69(7)
O(3)–Cs(1)–O(6F)	69.69(6)	O(3)–Cs(1)–O(5D)	72.86(6)
O(3)–Cs(1)–O(2)	53.38(6)	O(3)–Cs(1)–O(1A)	101.67(6)
O(3)–Cs(1)–O(1B)	109.25(6)	O(3)–Cs(1)–O(4D)	105.79(6)

Symmetry code: A = $(-x+1/2, y-1/2, -z+3/2)$, B = $(x-1/2, -y+1/2, z-1/2)$, C = $(-x, -y+1, -z+1)$, D = $(x, -y+1, z+1/2)$, E = $(x-1/2, y-1/2, z)$, F = $(-x+1/2, -y+1/2, -z+1)$.

another type of two-oxygen bridges along the *b*-axis. Viewed down the *a* axis, three kinds of oxygen bridges link six cesium cations to an irregular hexagon (figure 11).

3.6. *Thermal analysis*

All salts are dried in the vacuum before analysis. The decomposition process of **I** can be divided into two stages. The first stage with 17.57% mass loss is in agreement with the theoretical value of 17.10%, corresponding to loss of one NO_2 group. Then a rapid weight loss (60.08%) was observed from 325.83 to 344.00°C with loss of another NO_2 group and collapse of the pyridyl ring backbone. Complex **II** also has a rapid weight loss (30.84%) in the range of 296.59–335.19°C due to loss of two NO_2 groups.

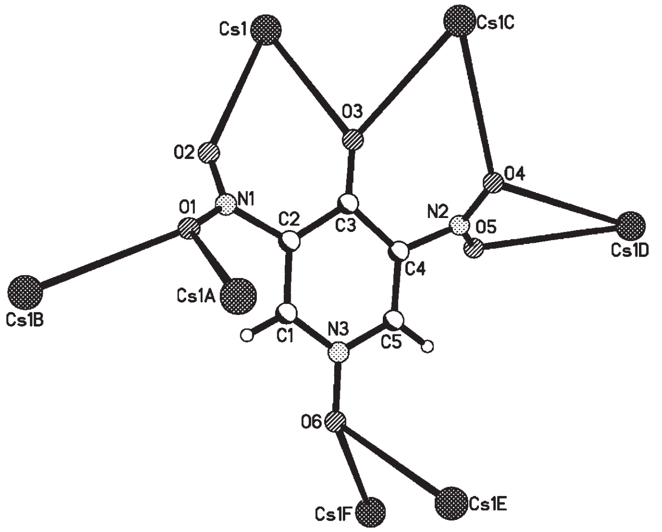

Figure 10. Coordination modes of 3,5-dinitro-4-pyridone-N-hydroxide anion toward cesium cations in **VI**.

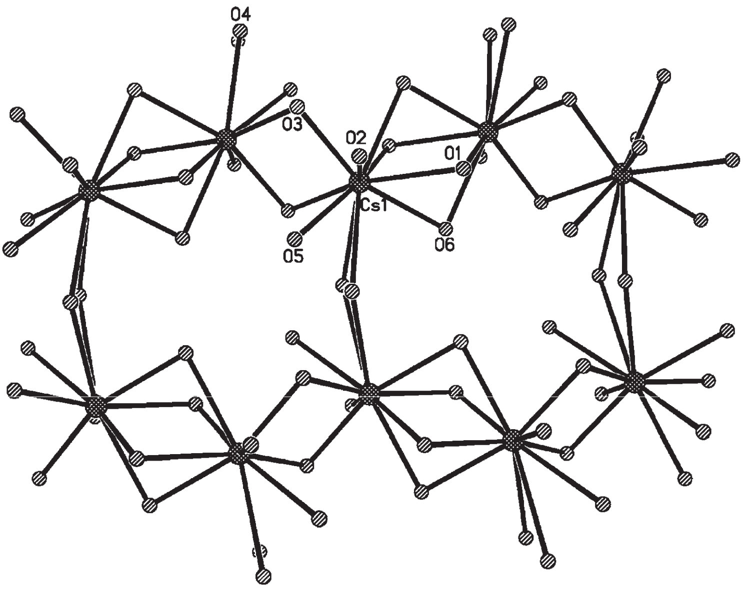

Figure 11. The extended array of complex **VI** formed by oxygen bridges coordinated to the cesium cations in the crystal. Only oxygen atoms linked with cations are maintained for clarity.

Complexes **III** and **IV** have the similar decomposition processes. First they lose one NO_2 group, and then an explosive decomposition occurred accompanying dramatic mass loss. Complex **V** has three stages in the decomposition process. The first and second stages from 156.30 to 254.64°C and 254.64 to 302.04°C with the weight loss of 16.93, 16.94%, respectively, correspond well with loss of NO_2 (16.10%). The third stage ceased at 921.72°C with weight loss of 46.93%. The decomposition of **VI** can be divided into two stages. The first stage has 26.83% mass loss, in agreement with the theoretical value of 27.63%, corresponding to loss of two NO_2 groups. The second stage between 288.73 and 861.37°C with weight loss of 54.82% accompanies the collapse of the pyridyl ring backbone.

4. Conclusions

Six rubidium and cesium compounds derived from dinitropyridone ligands are reported. The nitrogen donors of the pyridyl rings (N_{py}) displayed different linkage patterns to rubidium and cesium atoms. In Rb(2DNPO) (**I**), it links one metal atom; in **II**, there are extremely weak interactions between Cs^+ and N_{py}; but in **III** and **IV**, the N_{py} donors bridge between two metal cations. The bond distances between metal atoms and oxygen or nitrogen donors of the ligands vary in a wide range, some of which are very long, indicative of relatively weak interactions between Rb^+ or Cs^+ cations and the nitropyridone ligands. Aromatic π–π-stacking interactions exist only in **VI**. From these results, it is clear that these large alkali-metal cations enforce very little directional influence on the coordination geometry. The ion-ion, ion-dipole and other similar weak forces govern the geometrical configurations and lead to an aggregation of all polar groups in sheet-like domains covered by organic groups.

The thermogravimetric analyses of these complexes show the occurrence of consecutive processes: loss of NO_2 group, collapse of the pyridyl ring backbone and inorganic residue formation. The complexes **I** to **IV** have an explosive decomposition between 300 to 400°C, indicating their potential utility in solid propellants as lower toxic catalysts.

Supplementary material

Crystallographic data for the complexes are available upon request from the Cambridge Crystallographic Data center, 12 Union Road, Cambridge CB2 1EZ, UK, Fax: +44 1223 336 033; www: http://www.ccdc.cam.ac.uk or by Email from: deposit@ccdc.cam.ac.uk. Please quote the deposition numbers in all correspondence (CCDC Nos. 622104-622109, respectively).

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