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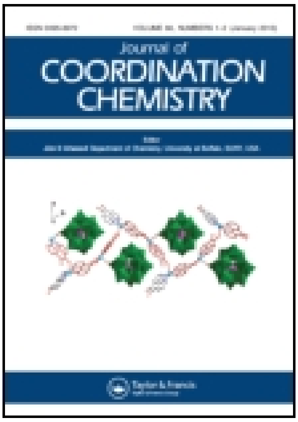

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Single-crystal X-ray studies of five alkali metal salts of luminol

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Single-crystal X-ray studies of five alkali metal salts of luminol

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Luminol salts of five alkali metals, Li, Na, K, Rb, and Cs, have been prepared and structurally characterized by single-crystal X-ray diffraction. Luminol is deprotonated at the same site whereas each ionic salt has a unique composition and a different number of water molecules. The cation/luminol ion pair to water molecule ratio in the lattices varies as follows: 1 : 0 for K, 1 : 1 for Li, 1 : 2 for Rb, 1 : 3 for Cs, and 1 : 6 for Na. The differences in composition among the five compounds lead to different metal coordination environments in the solid state and distinct 3-D molecular arrangements in the lattice.

Keywords: Luminol; Lithium; Sodium

Introduction

Luminol, 5-amino-2,3-dihydro-1,4-pthalazinedione [1], is well known as a material for the detection of traces of blood, for instance in forensic investigations [1–3]. The iron in hemoglobin powerfully catalyzes the oxidation of luminol by an oxidant (typically hydrogen peroxide) producing a vivid blue glow [4, 5]. The intense chemiluminescence of luminol makes it useful in bioanalytical chemistry for biosensing and in heavy metal detection (for instance, copper can be detected in sub-nM concentrations) [6, 7]. Chemiluminescence analysis has several advantages, such as simple instrumentation, low detection limits, large calibration range, and short analysis time [8].

In the USA, luminol is commonly sold and used as the neutral compound, whereas in China and Europe it is widely available as the sodium salt. The latter is marketed in the Russian Federation under the name "Galavit" [9]. Other names for luminol sodium salt dihydrate are "Tamerit" and "sodium nucleinate" [10]. Evidently, this salt has been used experimentally in treating inflammatory and autoimmune diseases, and as an immune modulator in cancer treatments [10, 11].

Despite the worldwide use and importance of luminol and the structural reports on 3-aminophthalhydrazide [12], apparently no structures of salts of luminol have been reported. Luminol itself is sparingly soluble in conventional organic solvents such as

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THF, ether, chloroform, and acetone. Good solvents for luminol are highly polar aprotic solvents such as DMSO and DMF. New luminol-linked calixarene derivatives have been prepared for the purpose of achieving good solubility of luminol. It has been found that luminol-linked calixarene derivatives are able to form host–guest complexes with organic compounds. However, most of these studies had to be performed in organic media due to the poor solubility of the functionalized calixarene in aqueous media [13]. Obviously, it is necessary to isolate luminol derivatives that possess specific chemiluminescent properties to apply to forensic detection in aqueous media.

Herein, we report on the five possible alkali metal salts of luminol, their syntheses and single-crystal X-ray structures. To our surprise, we find that each of the five alkali metal salts adopts a quite distinct and different crystal structure.

Results

The five diverse structures are shown as chemical drawings in scheme 1, whereas the details of single-crystal diffraction experiments are tabulated in table 1.

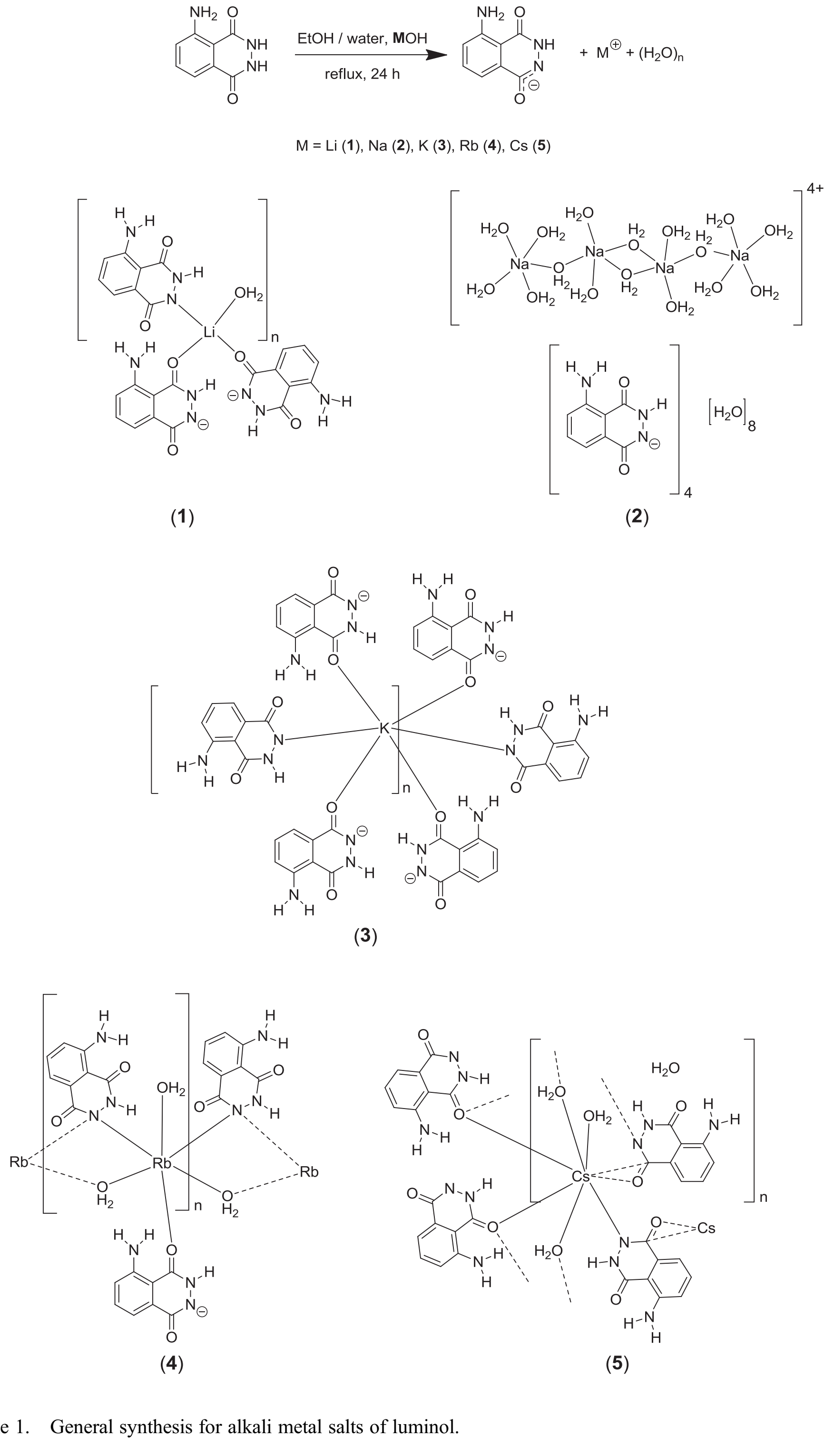
Crystal structure of the Li salt, 1

The solid-state structure of the Li luminol salt monohydrate is based on the content of the symmetry-independent unit of the crystal structure, with the smallest building block defined as $Li(L^-)(H_2O)$ (L^- is a deprotonated luminol), figure 1. The luminol ligand is mono-deprotonated at the 2-nitrogen of the diazine ring. Li^+ is predictably four coordinate. The tetrahedral coordination sphere of the metal includes three luminol monoanions and a water molecule, figure 2. The Li center is ligated by a different donor from each L^-: 1-oxygen in the first ligand, 4-oxygen in the second, and by the deprotonated 2-N from the diazine unit in the third. The Li–N and Li–O distances fall in the usual ranges as revealed by data mining in the Cambridge Structural Database [CSD, 14]. The Li–N bond length of 2.087(5) Å is expectedly longer than the Li–O bond distances, table 2. The Li–aqua distance is statistically indistinguishable from the Li–O (=C) bond lengths.

The most interesting part of this (and the others) crystal structure is the supramolecular arrangement of **1** generated by crystallographic symmetry elements. The structure contains five hydrogen bond donors and five hydrogen bond acceptors, thus four distinct hydrogen bonding interactions of the type N–H···O and O–H···O are established. The hydrogen bonding interactions link the cations, anions, and water molecules into 2-D sheets in the crystallographic *bc* plane. These sheets are separated by hydrophobic layers, and all layers stack up along the crystallographic *a* axis, figure 3.

Crystal structure of the Na salt, 2

The solid-state structure of **2** is decidedly more complex than that of **1**. The asymmetric unit contains two sodium cations, two mono-deprotonated luminol moieties, and 12 molecules of water, figure 4. Deprotonated luminols do not serve as ligands, thus the coordination environment of Na contains aqua ligands only. Each Na is five coordinate. A crystallographic inversion center generates the quadruply positively charged building blocks



Scheme 1. General synthesis for alkali metal salts of luminol.

Table 1. Crystallographic data and experimental details for **1–5**.

	1	**2**	**3**	**4**	**5**
Chemical formula	$C_8H_8LiN_3O_3$	$H_{32}Na_4O_{16}\cdot 4(C_8H_6N_3O_2)\cdot 8(H_2O)$	$C_8H_6KN_3O_2$	$C_8H_{10}N_3O_4Rb$	$C_8H_{12}CsN_3O_5$
M_r	201.11	1228.98	215.26	297.66	363.12
Crystal system, space group	Monoclinic, $P2_1/c$	Triclinic, $P\bar{1}$	Orthorhombic, $Pca2_1$	Monoclinic, $P2_1/c$	Orthorhombic, $Pna2_1$
Temperature (K)	296	100	100	100	100
a, b, c (Å)	13.0144(19), 9.5943(11), 7.3008(11)	7.952(2), 13.168(3), 13.734(3)	7.263(3), 8.652(4), 27.156(14)	18.413(9), 4.1238(15), 29.036(7)	10.926(4), 24.489(9), 4.5478(18)
α, β, γ (°)	90, 101.130(8), 90	74.180(14), 88.629(11), 82.050(17)	90, 90, 90	90, 96.88(3), 90	90, 90, 90
V (Å^3)	894.5(2)	1370.1(7)	1706.6(14)	2188.9(15)	1216.8(8)
Z	4	1	8	8	4
Radiation type	Cu Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα
μ (mm^{-1})	0.97	0.16	0.6	4.53	3.06
Crystal size (mm)	0.34 × 0.18 × 0.09	0.50 × 0.31 × 0.16	0.35 × 0.06 × 0.04	0.21 × 0.16 × 0.14	0.22 × 0.05 × 0.05
Diffractometer	Bruker SMART APEX2 area detector				
Absorption correction	Analytical with SADABS (Bruker-AXS, 2011)				
T_{min}, T_{max}	0.735, 0.918	0.926, 0.975	0.819, 0.977	0.450, 0.570	0.558, 0.860
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	12,524, 1656, 1279	39,175, 8357, 7630	25,327, 4224, 3767	41,212, 5542, 4577	27,842, 3721, 3492
R_{int}	0.046	0.018	0.044	0.042	0.028
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.054, 0.150, 0.99	0.030, 0.090, 1.03	0.033, 0.083, 1.04	0.040, 0.101, 1.03	0.016, 0.037, 1.04
No. of reflections	1656	8357	4224	5542	3721
No. of parameters	148	481	285	331	191
No. of restraints	2	0	13	16	13
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.28, −0.20	0.54, −0.19	0.44, −0.28	1.26, −1.01	0.37, −0.39
Absolute structure	–	–	Flack H D (1983), Acta Cryst. A39, 876–881	–	Flack H D (1983), Acta Cryst. A39, 876–881
Flack parameter	–	–	0.44(5)	–	0.000(13)

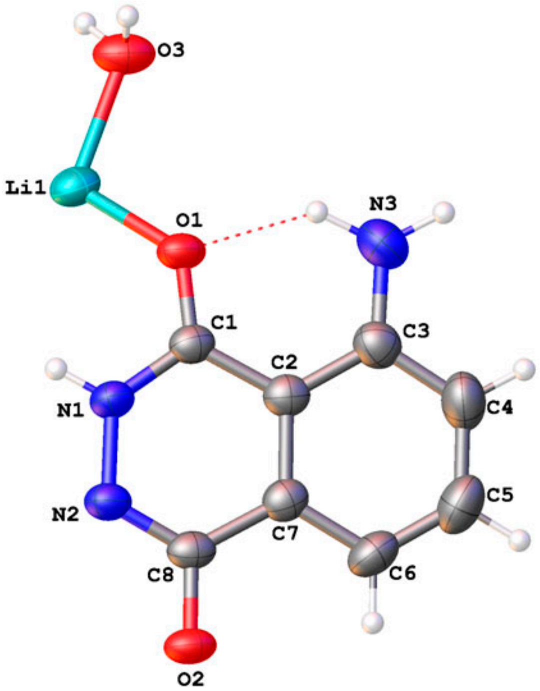


Figure 1. A molecular drawing of the asymmetric unit of **1** shown with 50% thermal probability ellipsoids.

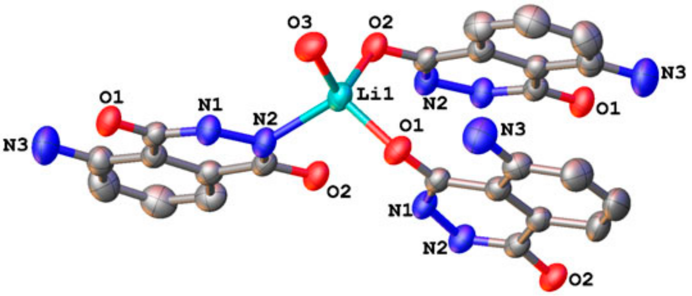


Figure 2. A molecular drawing of the Li coordination sphere in **1** shown with 50% thermal probability ellipsoids. All hydrogens are omitted.

$Na_4(H_2O)_{12}(\mu\text{-}H_2O)_4$ of the structure in which a Na (aqua)$_4$ unit containing Na1 is bridged by one aqua ligand to a Na(aqua)$_2$ unit of Na2, which in turn is linked to another Na (aqua)$_2$ unit of a symmetry-related atom Na2 with two μ_2-bridging aqua ligands, and a single bridging aqua ligand binds this Na2 to another Na (aqua)$_4$ unit of Na1, figure 5. Of course the inversion center also generates four additional equivalents of solvent water and two equivalents of luminol monoanions. All Li–O distances fall in the usual ranges according to a CSD search, table 2; the Na–O bond lengths to the terminal aqua ligands are on an average of 0.08 Å shorter than those to the bridging O atoms.

Table 2. Selected bond distances and angles in **1**–**5**, Å.

Compound **1**	
O(1)–Li(1)	1.933(5)
O(2)–Li(1) [*x*, −*y* + 1/2]	1.940(5)
O(3)–Li(1)	1.942(5)
N(2)–Li(1) [−*x* + 1, *y* −1/2, − *z* + 3/2]	2.087(5)
Compound **2**	
Na(1)–O(8)	2.2741(10)
Na(1)–O(5)	2.3203(10)
Na(1)–O(6)	2.3375(11)
Na(1)–O(7)	2.3738(10)
Na(1)–O(9)	2.4155(10)
Na(2)–O(12)	2.2681(10)
Na(2)–O(10)	2.3443(10)
Na(2)–O(9)	2.3696(10)
Na(2)–O(11)	2.3815(10)
Na(2)–O(11) [−*x* + 1, −*y* + 1, −*z* + 2]	2.4091(10)
Compound **3**	
K(1)–O(4)	2.659(2)
K(1)–O(3)#2	2.672(2)
K(1)–O(4) [*x* − 1/2, −*y* + 1, *z*]	2.676(2)
K(1)–O(3) [*x*, *y* + 1, *z*]	2.749(2)
K(1)–N(1)	2.879(3)
K(1)–N(1) [*x* − 1/2, −*y* + 1, *z*]	2.931(3)
K(1)–N(2)	3.407(3)
K(2)–O(2)	2.649(2)
K(2)–O(1) [*x* + 1/2, −*y* + 1, *z*]	2.663(2)
K(2)–O(2) [*x* + 1/2, −*y* + 2, *z*]	2.686(2)
K(2)–O(1) [*x*, *y* + 1, *z*]	2.751(2)
K(2)–N(4) [*x*, *y* + 1, *z*]	2.836(3)
K(2)–N(4) [*x* + 1/2, −*y* + 1, *z*]	2.921(3)
K(2)–N(5) [*x*, *y* + 1, *z*]	3.379(3)
Compound **4**	
Rb(1)–O(2) [−*x*, *y* + 1/2, −*z* + 1/2]	2.844(2)
Rb(1)–O(3)	2.872(3)
Rb(1)–O(3) [*x*, *y* − 1, *z*]	2.921(3)
Rb(1)–O(4)	3.023(3)
Rb(1)–N(1)	3.039(3)
Rb(1)–N(1) [*x*, *y* + 1, *z*]	3.085(3)
Rb(1)–O(8D)	3.238(16)
Rb(1)–N(2)	3.376(3)
Rb(1)–C(1)	3.619(3)
Rb(2)–O(7)	2.844(3)
Rb(2)–O(8C)	2.882(14)
Rb(2)–N(4)	2.970(3)
Rb(2)–O(7) [*x*, *y* − 1, *z*]	2.979(3)
Rb(2)–O(8A)	3.025(7)
Rb(2)–O(8A) [*x*, *y* − 1, *z*]	3.041(7)
Rb(2)–O(6) [−*x* + 1, − *y*, − *z* + 1]	3.050(2)
Rb(2)–N(4) [*x*, *y* + 1, *z*]	3.071(3)
Rb(2)–O(5)	3.143(3)
Rb(2)–C(9)	3.332(3)
Rb(2)–O(8C) [*x*, *y* − 1, *z*]	3.546(14)
Rb(2)–N(5) [*x*, *y* + 1, *z*]	3.566(3)
O(8C)–Rb(2) [*x*, *y* + 1, *z*]	3.546(14)
Compound **5**	
Cs(1)–O(1)	3.028(2)
Cs(1)–O(3)	3.0995(18)
Cs(1)–O(1) [*x*, *y*, *z* − 1]	3.106(2)
Cs(1)–O(4)	3.1794(18)

(*Continued*)

Table 2. (*Continued*).

Compound **5**	
Cs(1)–N(2) [*x* + 1/2, −*y* + 1/2, *z*]	3.306(3)
Cs(1)–O(3) [*x* − 1/2, −*y* + 1/2, *z*]	3.3750(18)
O(2)–Cs(1) [*x* − 1/2, −*y* + 1/2, *z* + 1]	3.6239(18)
O(5)–Cs(1) [−*x* + 2, −*y* + 1, *z* + 1/2]	3.732(2)
N(2)–Cs(1) [*x* − 1/2, −*y* + 1/2, *z* + 1]	3.381(3)
N(3)–Cs(1) [*x* − 1/2, −*y* + 1/2, *z*]	3.8416(19)

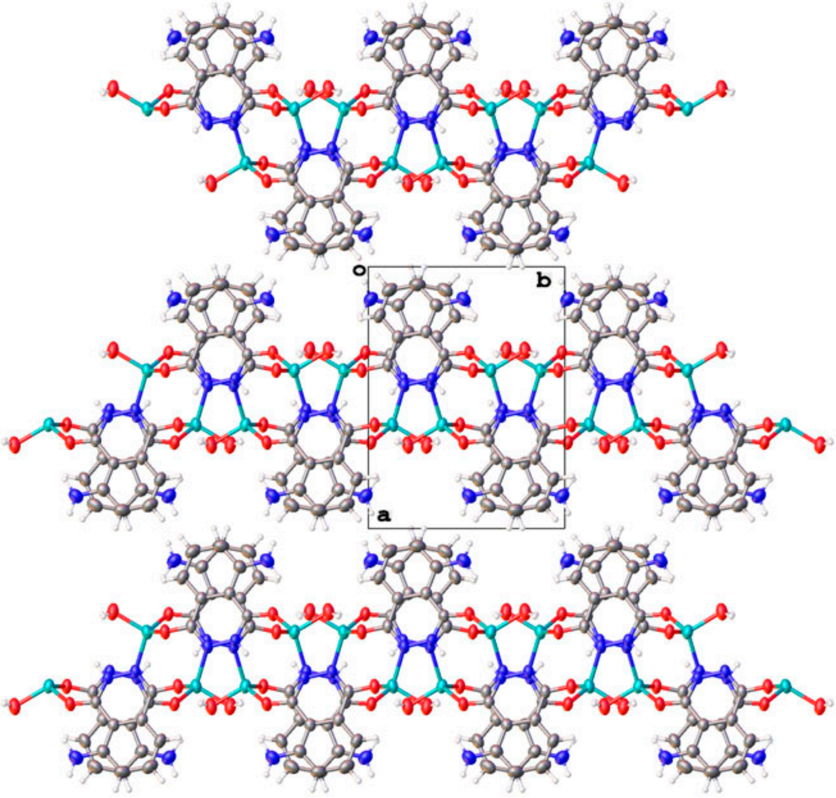


Figure 3. A packing diagram of **1** viewed along the crystallographic *c* axis.

The supramolecular arrangement of charged and neutral species in the lattice of **2** is spectacularly complicated. There are 30 hydrogen bonding donors and 20 acceptors; 24 unique hydrogen bonding interactions of types O–H···O, O–H···N, and N–H···O are observed. The hydrogen bonds range from medium to strong and link the cations to form 2-D hydrophilic networks parallel to the crystallographic *ac* plane, and the anions to form 2-D networks parallel to the hydrophilic networks, and these sheet-like networks are connected by hydrogen bonds to form a 3-D framework, figure 6.

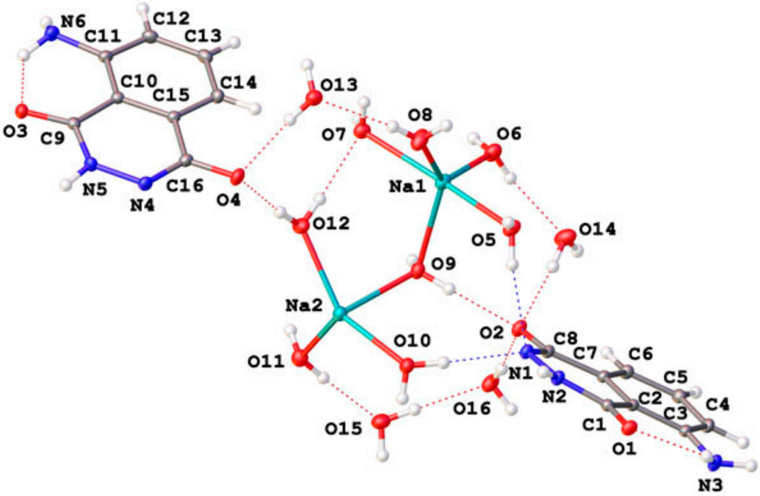


Figure 4. A molecular drawing of the asymmetric unit of **2** shown with 50% thermal probability ellipsoids.

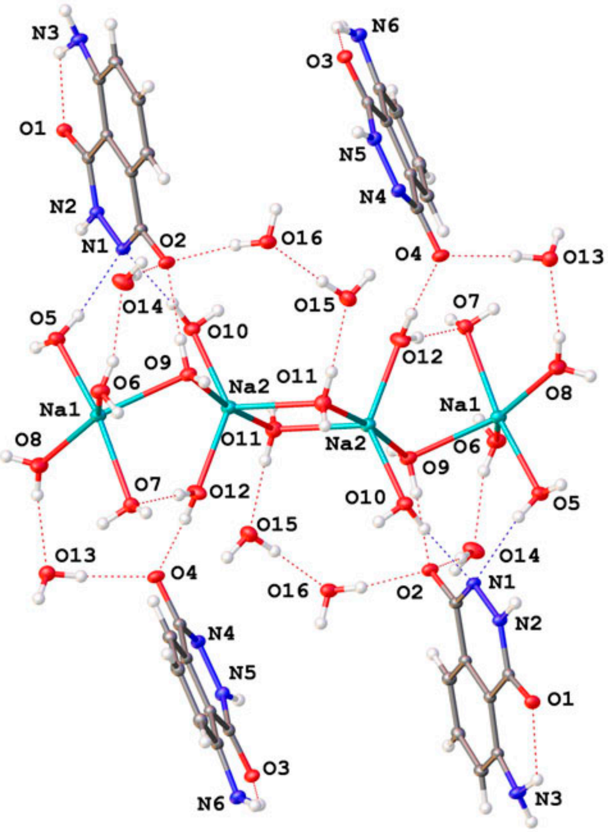


Figure 5. A molecular drawing of the basic structural unit in the lattice of **2** shown with 50% thermal probability ellipsoids.

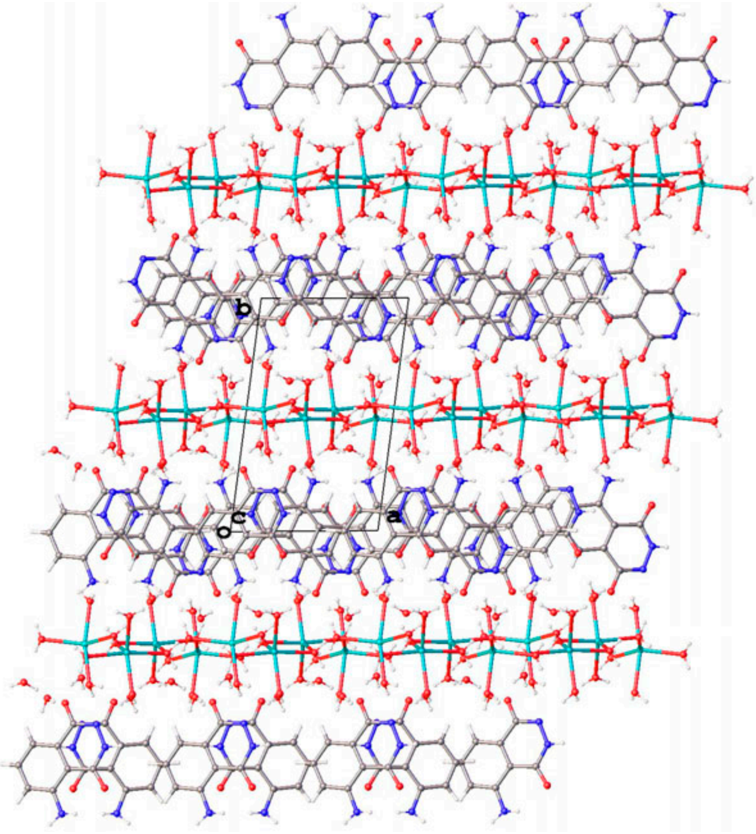


Figure 6. A packing diagram of **2** viewed along the crystallographic *c* axis.

Crystal structure of the K salt, 3

The solid-state structure of the potassium congener of **1** and **2**, in contrast to those of Li and Na, does not contain any aqua ligands or crystallization water. The asymmetric unit is comprised of two potassium cations and two luminol monoanions, figure 7. Each K cation resides in a distorted octahedral environment formed by six luminol monoanion ligands;

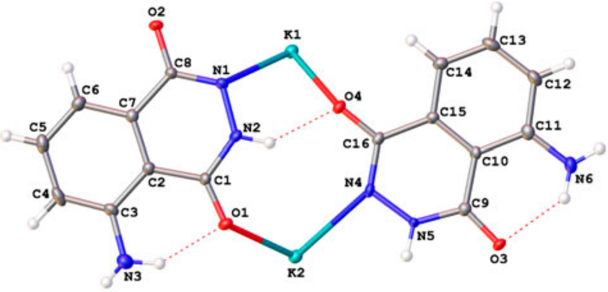


Figure 7. A molecular drawing of the asymmetric unit of **3** shown with 50% thermal probability ellipsoids.

each metal center binds to four O and two deprotonated N at the 2-positions of the luminol monoanions, figure 8. The K–N distances average 2.89(4) Å and are statistically significantly longer than the K–O distances (av. 2.69(4) Å), table 2. There are six hydrogen donors and eight hydrogen bond acceptors in the structure. There are six unique weak hydrogen bonding interactions of the N–H···O kind as judged by the suboptimal

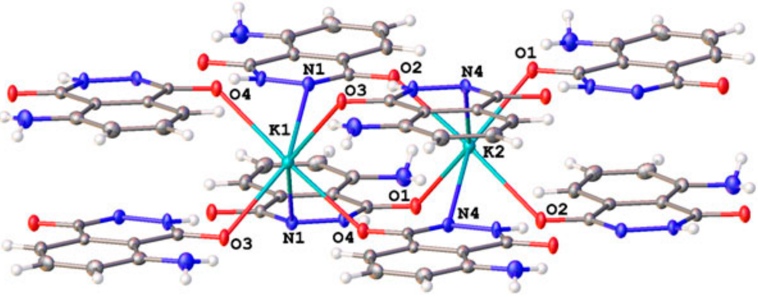


Figure 8. A molecular drawing of the coordination environments of K in **3** shown with 50% thermal probability ellipsoids.

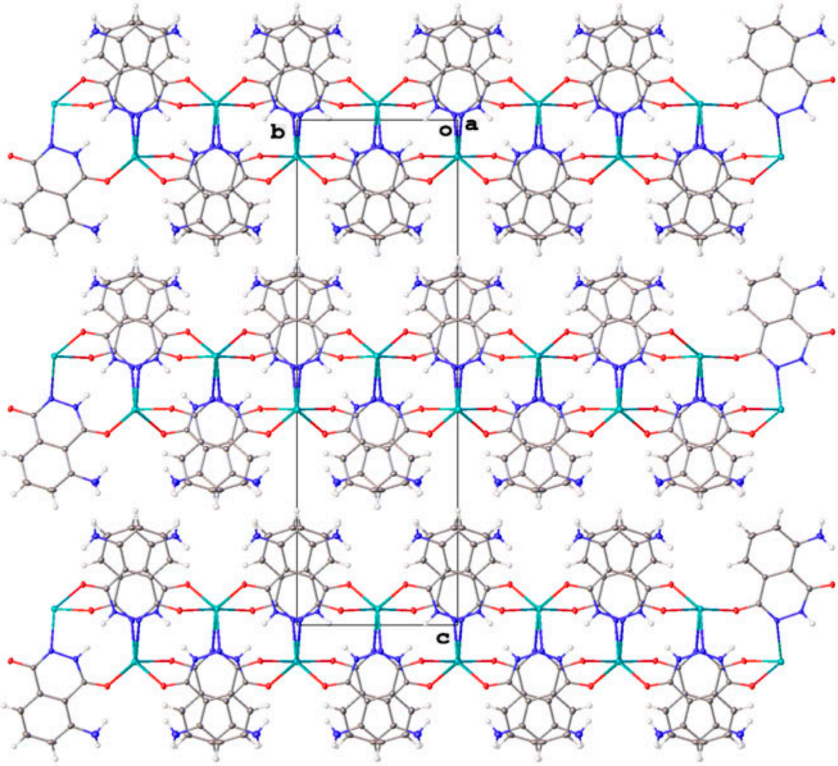


Figure 9. A packing diagram of **3** viewed along the crystallographic *a* axis.

donor–H···acceptor angles in the range 135–145°, and one weak N–H···N hydrogen bonding interaction characterized by a favorable angle of 171(3)°, but a rather long N···N separation of 3.351(4) Å. The word interaction describes these donor–H···acceptor contacts better than the term "bond." The K and luminol monoanions bind to each other to form 2-D sheets in the *ab* crystallographic plane; these sheets are connected into a 3-D framework along the crystallographic *c* axis with attractive N–H···N contacts, figure 9. Luminol monoanions in the structure are disordered over two positions with minor components of the disorder present 4% of the time. The structural discussion was based only on the major component of the disorder.

Crystal structure of the Rb salt, 4

In the solid state of the Rb luminol complex, a larger alkali metal, aqua ligands are present; the asymmetric unit contains two Rb cations, two luminol monoanions, as usual deprotonated at the 2-position, and four aqua ligands; one of the latter is disordered over four positions labeled O8(a–d) in a 0.389(3) : 0.265(5) : 0.179(5) : 0.166(5) ratio, figure 10. It was not possible to locate the hydrogens on the disordered O8. The disorder affects the composition of the coordination environments of the two metals. In three of the four disorder positions, water coordinates to Rb and in one simply fills a lattice void.

Rb1 is the more coordinatively saturated metal in this structure, ligated by three luminol monoanions through 2-N in the first ligand, through 4-oxygen in the second, and to 2-N and 3-N in the third. The latter ligand employs its delocalized π cloud to coordinate to the metal, unlike the other ligands in the structure. The Rb1–N1 distance to the first ligand, where N1 ligates with its in-plane lone pair is 3.085(3) Å, whereas the Rb1–N1 distance to the π-donative N atom in the third ligand is shorter at 3.039(3) Å. The Rb1–N2 distance to

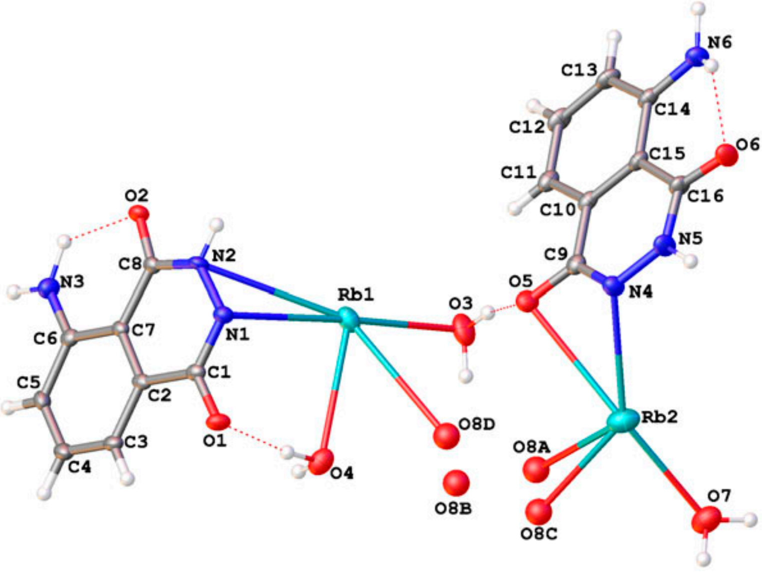


Figure 10. A molecular drawing of the asymmetric unit of **4** shown with 50% thermal probability ellipsoids.

the 3-nitrogen in the third ligand is decidedly longer at 3.376(3) Å; the kind of interaction is open to interpretation, but we interpret it as a dative bond. Other selected bond distances are tabulated in table 2 and fall within the usual ranges according to a CSD search. Three other coordination sites about Rb1 are fully occupied by one terminal and two bridging aqua ligands, but the occupancy of the eighth coordination site varies between zero and 16.6(5)%, depending on whether the disordered aqua ligand is present. Thus, Rb1 is either seven or eight coordinate, figure 11.

Rb2 is always coordinated by three luminol monoanions (through 1-oxygen in one, 2-nitrogen in another, and by 1-oxygen and 2-nitrogen in the third) and two fully occupied aqua ligands, in six coordinate. The seventh and eighth sites are occupied by the disordered aqua and at each of the two sites the occupancy of the aqua ligand varies between zero and 38.9(3)%. This metal center can be six, seven, or eight coordinate, figure 12.

The supramolecular structure is dominated by two types of hydrogen-bonded columns, figure 13. The first type contains only Rb1 that are bridged by one aqua ligand and 2-nitrogen of one luminol monoanion. The second type of column contains only Rb2 bridged by an aqua ligand, 2-nitrogen of luminol monoanions, and a partially occupied aqua ligand. The columns are parallel to one another and propagate along the crystallographic *b* axis. Accordingly, the basic motif in this structure is 1-D. The columns are connected by O–H···O and O–H···N hydrogen bond interactions to form a 3-D framework of hydrogen bonds. The voids between columns are sometimes occupied by solvent water, which resides in them 26.5(5)% of the time.

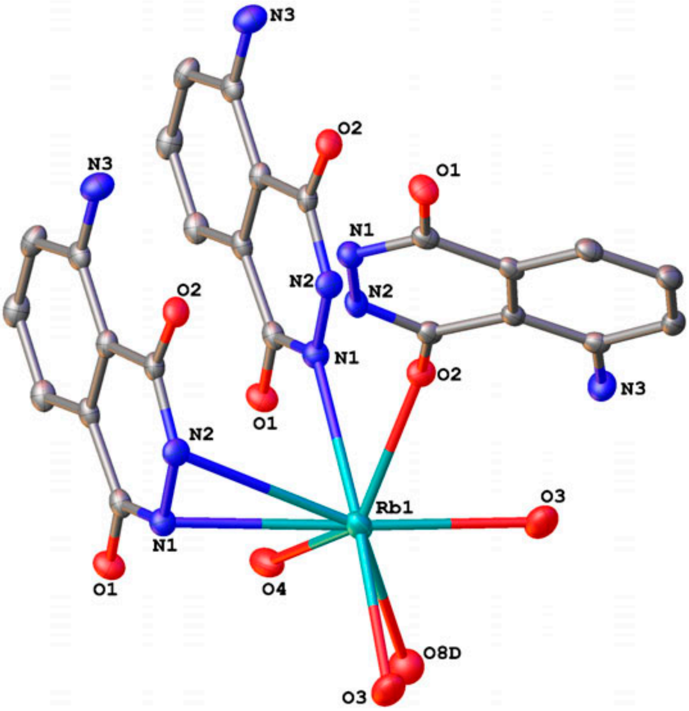


Figure 11. A molecular drawing of the coordination environment of Rb1 in **4** shown with 50% thermal probability ellipsoids.

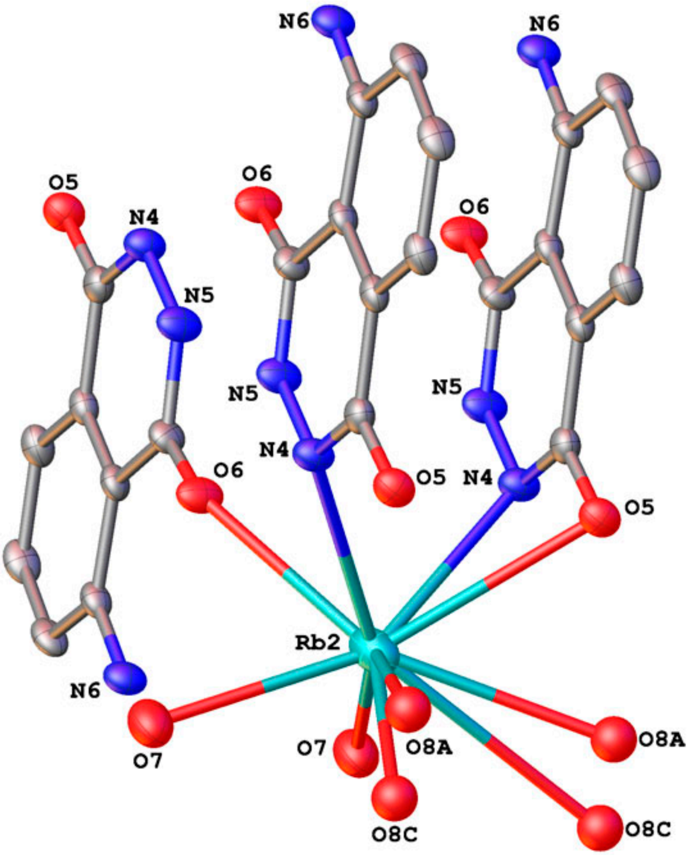


Figure 12. A molecular drawing of the coordination environment of Rb2 in **4** shown with 50% thermal probability ellipsoids.

Crystal structure of the Cs salt, 5

The asymmetric unit of this structure contains one Cs cation, one luminol monoanion, deprotonated at the 2-position, and three water molecules, two of which serve as aqua ligands and one as a co-crystallant that fills lattice cavities, figure 14. The coordination sphere of the large Cs is comprised of three aqua ligands and four luminol monoanions. Two of the anions coordinate with 4-oxygen, one with 2-nitrogen, and one binds in a "slipped" η^3-mode or at least with the p-orbitals of O2 (1-oxygen) and N2 (2-nitrogen) of the luminol ring. In figure 15, Cs1 is depicted as eight coordinate. One of the luminol monoanions bridges two Cs^+ with a 4-oxygen to form a zigzag Cs–O–Cs–O chain in the crystallographic *c* direction. In 3-Ds (figure 16), the cations, anions, and aqua ligands form hydrogen bonds to make 2-D sheets that are parallel to the crystallographic *ac* plane. The sheets are reinforced by O–H···O and N–H···O hydrogen bonds. The sheets are stacked along the crystallographic *b* axis and are linked by O–H···O and O–H···N hydrogen bonds that invariably involve solvent water. There are no direct hydrogen bonding interactions between adjacent sheets.

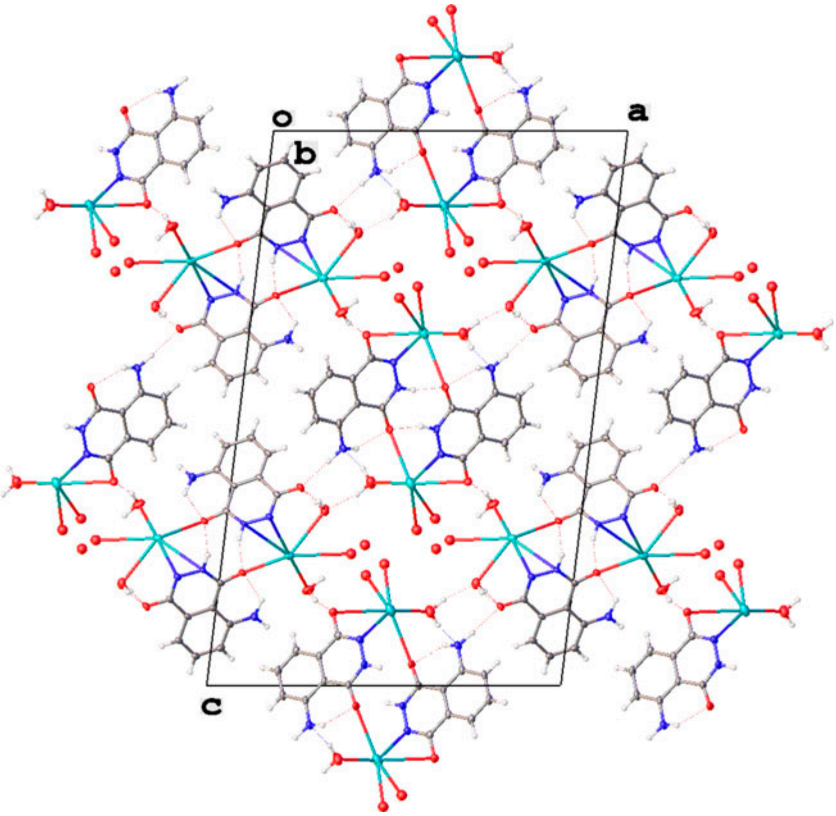


Figure 13. A packing diagram of **4** viewed along the crystallographic *b* axis.

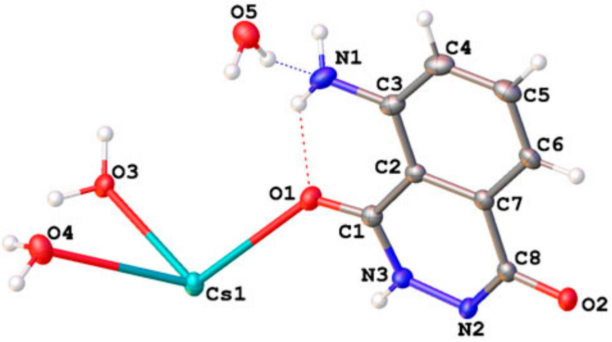


Figure 14. A molecular drawing of the asymmetric unit of **5** shown with 50% thermal probability ellipsoids.

Structure comparison and discussion

It is instructive to analyze the five structures of the five alkali metals for similarities and differences. The composition of the five compounds is different as revealed by the ratio of

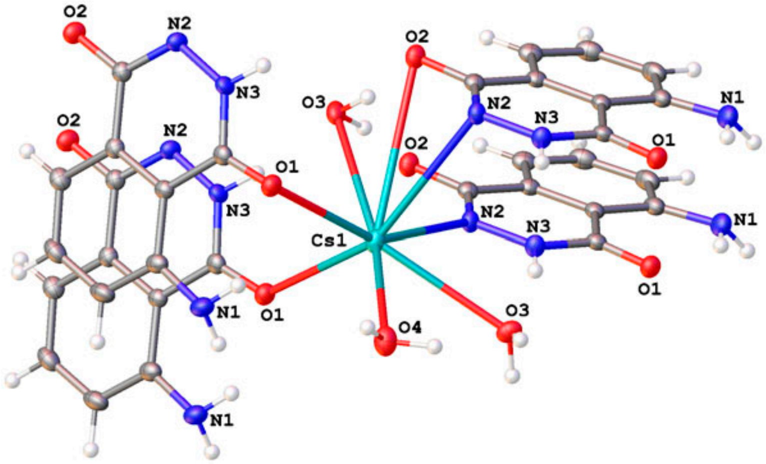


Figure 15. A molecular drawing of the Cs coordination environment in **5** shown with 50% thermal probability ellipsoids.

cation/anion pairs to the number of water molecules in the lattices: it is 1 : 0 for K, 1 : 1 for Li, 1 : 2 for Rb, 1 : 3 for Cs, and 1 : 6 for Na. The coordination environment of the metals may include luminol monoanions only (K), aqua ligands only (Na), or a mixture of the two. Predictably, as the metals become progressively larger from Li^+ to Cs^+ their coordination numbers increase from four for Li to eight for Cs. The metal–oxygen and metal–nitrogen distances also increase, consistent with the larger metal sizes and coordination number (usually the higher the coordination number, the longer the bonds). In all the cases the bond distances are unexceptional, according to our CSD searches.

Luminol is always present as a monoanion deprotonated at the 2-nitrogen site, which is characteristic of the compound in the solid state. The luminol monoanion exhibits a variety of coordination modes, and serves as a O- or N-monodentate terminal ligand, μ_2-bridging ligand with either a nitrogen or oxygen, a bridging ligand with two oxygens, and can also ligate in η^2- and η^3-fashion to larger metals that have diffuse electron clouds (Rb and Cs).

In all structures, hydrogen-bonding interactions abound with three types O–H···O, O–H···N, and N–H···O formed between luminol mononions, aqua ligands, and solvent water molecules, when such are present. The directional hydrogen-bonding interactions range from weak (in **3**) to medium to strong, and the latter are frequently charge assisted.

The bulk crystal quality was typically low and it was difficult to isolate crystals of high quality for the crystallographic experiments, whereas the small crystals selected for the single-crystal diffraction data collection produced high-quality data. Undoubtedly, the hydrogen-bonding interactions reinforce the lattice and make the crystals stable. In Rb structures, there are 1-D columns, whereas 2-D networks can be distinguished in the other four cases. In all structures, hydrogen bonds link these units to form spectacular hydrogen-bonding networks throughout the crystal.

The number of water molecules varies and thus, it is difficult to, a priori, predict the crystal composition or ligand coordination mode. The most common motif is sheet structures in which metals are bridged in a μ_2-fashion by a ligand, observed in four out of five structures.

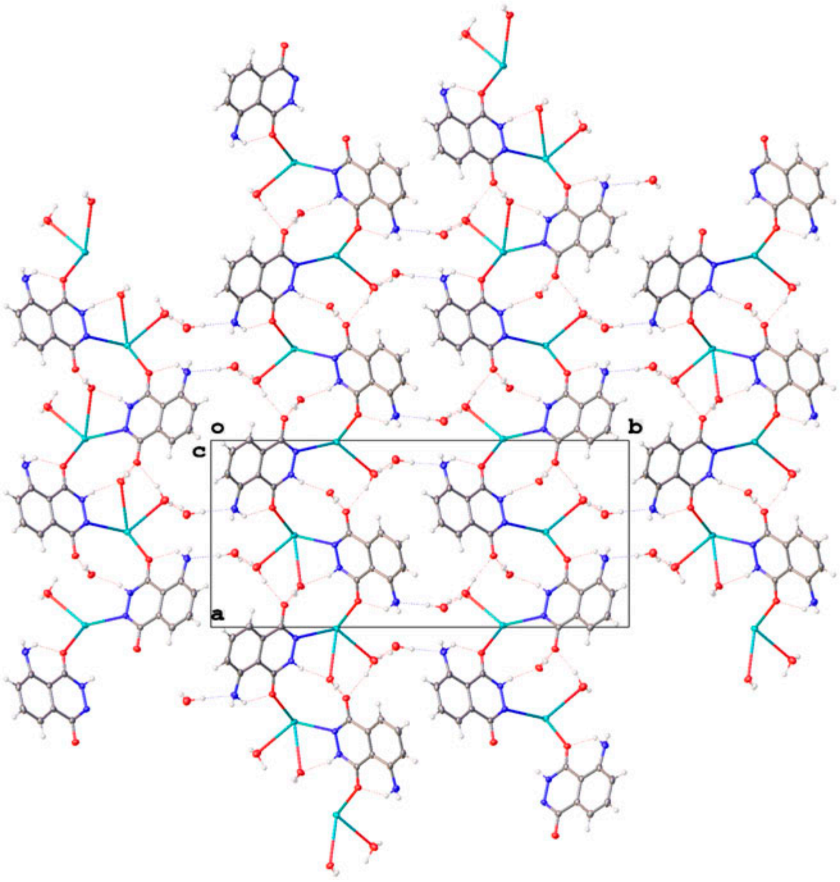


Figure 16. A packing diagram of **5** viewed along the crystallographic *c* axis.

Conclusions

Five luminol salts of Li, Na, K, Rb, and Cs have been prepared and characterized by single-crystal X-ray analysis. The compositions of the five crystal structures are different, with the cation/luminol anion pair to the number of waters ratio in the lattices varying as follows: 1 : 0 for K, 1 : 1 for Li, 1 : 2 for Rb, 1 : 3 for Cs, and 1 : 6 for Na. The metal coordination environment includes luminol monoanions only (K), aqua ligands only (Na), or a mixture of the two. The 3-D structures of the salts are different. The diversity of the coordination chemistry of these seemingly simple luminol salts should facilitate further studies of luminol chemistry.

Experimental

Synthesis of alkali metal luminol salts. To 2.0 g of luminol (Aldrich Chem. Co.) dispersed in ethanol (100 mL) was added 1.2 equiv. of the metal hydroxide (50%, w/w aqueous solution). The mixture was refluxed for a day and then allowed to stir at room temperature for another day. Finally, the suspension was filtered through a glass frit and the powder was recrystallized from water. (In case of rubidium salts, crystallized from mixture of EtOH/water (1 : 1 v/v)). For **1**, **2**, **3**, **4**, and **5**: colorless crystals, Yield: over 95%, ^{1}H NMR (300.133 MHz, D_2O): δ 7.25 (t, 2H), 7.043 (d, 1H), 6.67 (d, 1H), 4.642 (s, **1** = 5H; **2** = 14H; **3** = 5H; **4** = 6H; **5** = 6H). ^{13}C NMR (75.403 MHz, D_2O): δ 112.649, 114.106, 118.152, 130.836, 133.848, 148.937, 161.146, 162.023.

Crystallographic experiment. A typical experiment is described for **1**. A colorless crystal with approximate dimensions 0.34 × 0.18 × 0.09 mm^3 was selected under oil at ambient conditions and attached to the tip of a MiTeGen MicroMount©. The crystal was mounted at room temperature and centered in the X-ray beam by using a video camera.

The crystal evaluation and data collection were performed on a Bruker SMART APEXII diffractometer with Cu Kα (λ = 1.54178 Å) radiation and the diffractometer to crystal distance of 4.03 cm.

The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 50 frames collected at intervals of 0.5° in a 25° range about ω with the exposure time of 10 s per frame. The reflections were successfully indexed by an automated indexing routine built in the APEXII program. The final cell constants were calculated from a set of 3178 strong reflections from the actual data collection.

The data were collected by using the full sphere data collection routine to survey the reciprocal space to a resolution of 0.82 Å. A total of 12,524 data were harvested by collecting 19 sets of frames with 0.6° scans in ω with an exposure time 20–40–60 s per frame. These highly redundant data-sets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements [15].

Structure solution and refinement

The systematic absences in the diffraction data were uniquely consistent for the space group $P2_1/c$ that yielded chemically reasonable and computationally stable results of refinement [16–19].

A successful solution by direct methods provided most non-hydrogen atoms from the E-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All aromatic hydrogens were included in the structure factor calculation at idealized positions and allowed to ride on the neighboring atoms with relative isotropic displacement coefficients.

There is also one molecule of solvent water in the asymmetric unit.

The final least-squares refinement of 148 parameters against 1656 data resulted in residuals R (based on F^2 for $I \geq 2\sigma$) and wR (based on F^2 for all data) of 0.0536 and 0.1500, respectively. The final difference Fourier map was featureless.

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