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Luminescence properties of three structures built from 3-cyano-4-dicyanomethylene-5-oxo-4,5-dihydro-1*H*-pyrrol-2-olate and alkaline metals (Na, K and Rb)

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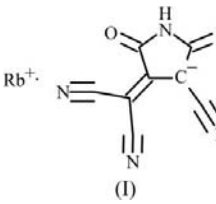
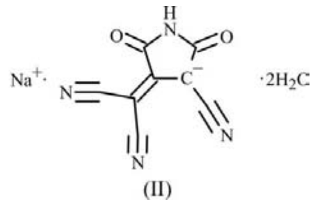
The structures of three salts of 3-cyano-4-dicyanomethylene-5-oxo-4,5-dihydro-1*H*-pyrrol-2-olate with alkali metals (Na, K and Rb) are related to their luminescence properties. The Rb salt, rubidium(I) 3-cyano-4-dicyanomethylene-5-oxo-4,5-dihydro-1*H*-pyrrol-2-olate, $Rb^+\cdot C_8HN_4O_2^-$, is isomorphous with the previously reported potassium salt. For the Na compound, sodium(I) 3-cyano-4-dicyanomethylene-5-oxo-4,5-dihydro-1*H*-pyrrol-2-olate dihydrate, $Na^+\cdot C_8HN_4O_2^-\cdot 2H_2O$, two independent sodium ions, located on inversion centers, are coordinated by four water molecules each and additionally by two cyano groups for one and two carbonyl groups for the other. The luminescence spectra in solution are unaffected by the nature of the cation but vary strongly with the dielectric constant of the solvent. In the solid state, the emission maxima vary with structural features; the redshift of the maximum luminescence varies inversely with the distance between the stacked anions.

Comment

Crystal engineering of organic and organometallic molecules involves, among other things, an understanding of the relationship between individual molecules and the properties of their crystals. Such an understanding is necessary in the search for new materials with useful properties (Shirota, 2000; Law, 1993; Hung & Chen, 2002). Luminescent organic and organometallic compounds have attracted attention because of their potential application in organic light-emitting devices (Wang, 2001; Kido & Okamoto, 2002; The Special Issue on Organic Electronics, 2004). Recently, it was shown (Tafeenko *et al.*, 2007) that the luminescence of compounds based on the title anion 3-cyano-4-dicyanomethylene-5-oxo-4,5-dihydro-1*H*-pyrrol-2-olate (*A*) covers a wavelength range from UV to red. Tuning of the emission photon energy can be achieved through changes in intermolecular interactions or/and chemical modification of the anion. The first of these two approaches was used in this work. Some types of intermolecular contacts were found to be of special importance for optical and other electronic properties of organic or metal–organic crystals. In particular, side-by-side (SS, for example, in the case of π-conjugated organic molecules and polymers) and face-to-face contacts (FF, in stacks) are generally recognized as important factors in the control of electron transport and optical properties of molecular crystals. Our previous studies (Tafeenko *et al.*, 2007, and references therein) have shown that the FF interaction is an intrinsic property of anion *A*. Therefore, by modifying the distance between neighboring anions, we intended to address the question of how the luminescence maximum depends on the stacking arrangement of *A*. Thus, three salts of *A* with alkali metals [Na, *i.e.* title compound (II), K and Rb, *i.e.* title compound (I)] were prepared. The structure of the potassium salt, presented earlier (Tafeenko *et al.*, 2003), possesses structural features that we expected would permit a systematic variation of the anion stacking distance. In the potassium salt, all exocyclic heteroatoms of *A* are involved in the formation of a nearly ideal tricapped trigonal prism that encloses the cation, and the anions are arranged in stacks as a result of π–π interactions.



(I)



(II)

We intended to include cations of different ionic radius into the tricapped trigonal prism, thus varying its volume and with it the distance between adjacent anions in the stack. We succeeded in preparing an isomorphous salt in the case of Rb (Fig. 1 and Table 1) but failed for sodium. For Rb, as with the potassium salt, all external atoms of anion *A* are involved in the formation of the tricapped trigonal prism. Each prism is

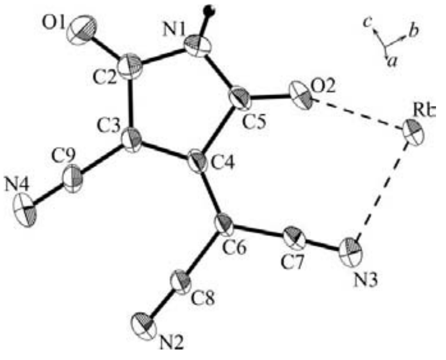


Figure 1
The atom numbering in the rubidium salt, with displacement ellipsoids drawn at the 50% probability level.

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connected to two neighboring prisms *via* a common base and to two other prisms *via* common edges. Thus, double channels are formed along the *a* axis, in which two rows of rubidium cations are located (Fig. 2). The shortest distance between cations in a given row is 4.2753 (5) Å, while the shortest distance between cations located in different rows is 5.0455 (7) Å. The cation–apex distances in the tricapped prism vary in the range 2.833 (1)–3.173 (2) Å in the potassium salt, while for the rubidium salt the range is 2.964 (2)–3.271 (3) Å. The edge lengths in the rubidium salt are also larger, and as a result, the stacking distance for the anions is larger for Rb than for the K salt [3.430 (5) and 3.388 (2) Å, respectively]. The hydrogen bonding between anions *A* also changes. In the potassium salt, anions *A* are connected by an N—H···O hydrogen bond, which is rather weak [H···O = 2.31 (2) Å and N—H···O = 151 (2)°], while the rubidium salt exhibits an even weaker contact [H1···O1^{vii} = 2.49 (5) Å and N1—H1···O1^{vii} = 150 (4)°; symmetry code: (vii) $-x, y+\frac{1}{2}, -z+\frac{1}{2}$].

It was found to be more difficult to prepare single crystals of the Na salt as well as to index the powder pattern. It appeared that the *causa proxima* was the simultaneous precipitation of several phases. Slow evaporation of a water–ethanol solution at 323 K yielded a small crystal suitable for X-ray measurements. Two independent Na atoms, *viz*. Na1 and Na2, occupy inversion centers. Their coordination environments consist of four water molecules plus two cyano (Na1) or two carbonyl (Na2) groups, with similar geometry for both (Table 2). The geometry of *A* is essentially the same as in the previously studied structures. The angle between the $-C(CN)_2$ group and the five-membered ring is 2.1 (1)°. Cation *A* links the two Na atoms *via* the C9/N4 cyano group and the C5/O2 carbonyl group (Figs. 3 and 4) to form an infinite chain running along [021]. Each anion is linked to its neighbor by N—H···O hydrogen bonds, thus forming a centrosymmetric dimer (Fig. 5 and Table 3). Although adjacent dimers are packed in a fashion similar to that found in the ammonium salt (Tafeenko *et al.*, 2005), the arrangement of the dimers is somewhat different. In the ammonium salt, adjacent dimers are connected by (–C—N)···(N—C–) dipole–dipole and π–π interactions, thus forming infinite planar ribbons, while for the

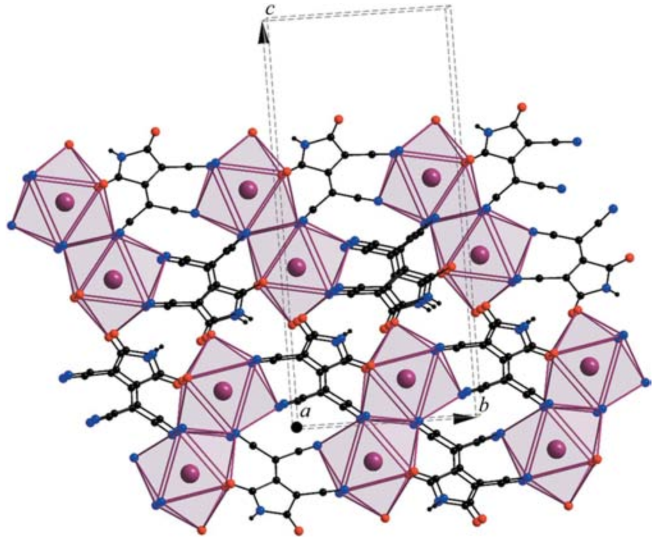

Figure 2
The packing of the rubidium salt, viewed along the *a* axis, showing the coordination of the cations by the stacked anions.

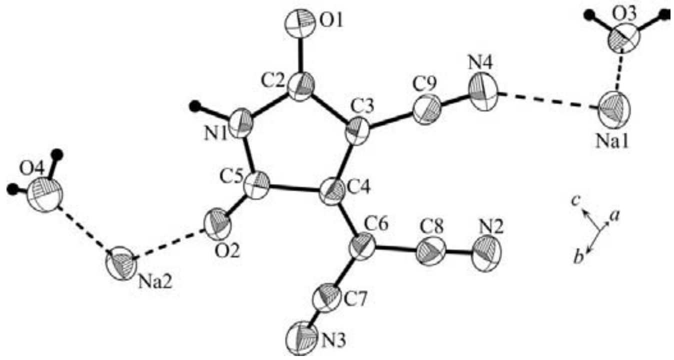

Figure 3
The atom numbering in the sodium dihydrate salt, with displacement ellipsoids drawn at the 50% probability level. Atoms Na1 and Na2 are located at inversion centers.

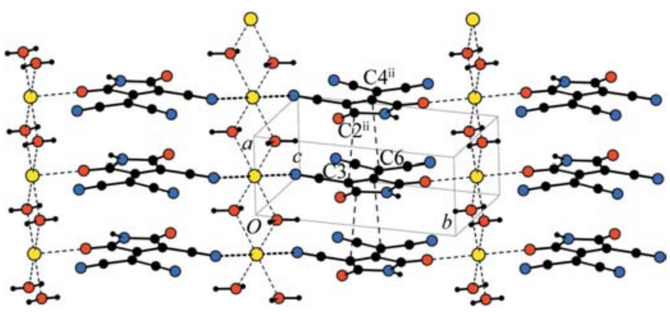

Figure 4
Part of the crystal structure of the sodium salt, showing infinite anion–cation chains. Adjacent chains are connected by coordinated water molecules and π–π interactions between anions. The shortest distances between atoms of neighboring anions are 3.256 (5) (for C3—C2^{ii}) and 3.272 (4) Å (for C6—C4^{ii}) [symmetry code: (ii) $x+1, y, z$].

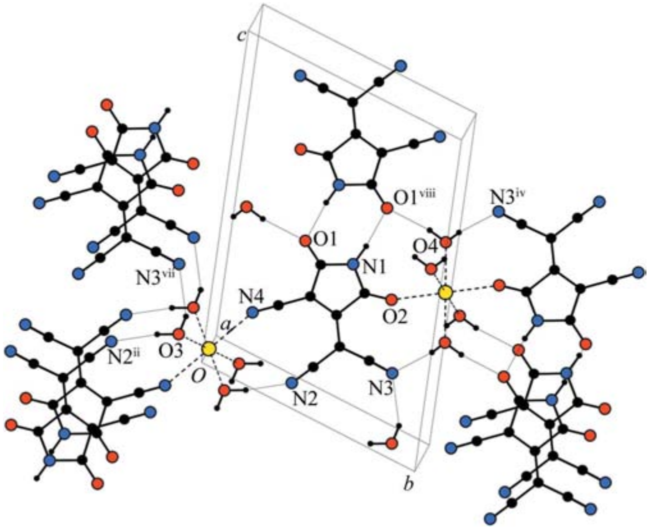

Figure 5
Hydrogen bonds (thin lines) in the structure of the sodium salt. See Table 3 for symmetry codes.

sodium salt the packing pattern is mediated by hydrogen bonding between cyano groups of the dicyanomethylene group and coordinated O3 water molecules (Fig. 5). The separation between stacked anions is 3.231 (3) Å [for the ammonium salt the distance is larger at 3.358 (2) Å].

Luminescence spectra of the sodium, potassium and rubidium salts were recorded in different solvents and in the solid state. In solution, the spectra are unaffected by the nature of the cation but vary depending on the dielectric constant of the solvent. The dielectric constants are 19.41, 20.56, 46.45 and 78.30 (Akhadov, 1999) for 2-propanol, acetone, dimethyl sulfoxide and pure water, respectively. An increase in the dielectric constant of the solvent results in a redshift of the luminescence from 504 to 539 nm (Fig. 6). In the solid state, the redshift of the luminescence maximum rises sharply for all of the salts studied. As mentioned above, the distances between the anions in the stacks of the sodium, ammonium, potassium and rubidium salts are 3.231 (3), 3.358 (2), 3.388 (2) and 3.431 (5) Å, respectively. The correlation between these values and the luminescence maxima is clear – the smaller the distance, the larger the redshift of the luminescence maximum (Fig. 7).

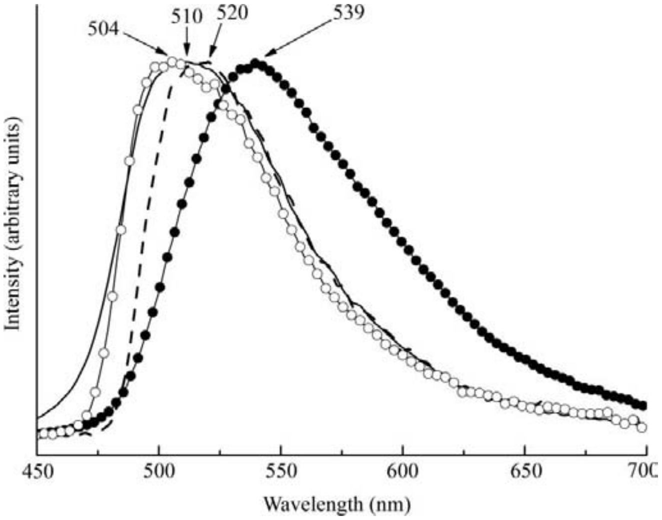

Figure 6
Luminescence spectra of the potassium salt solutions in different solvents: water (filled circles, maximum 539 nm), dimethyl sulfoxide (broken line, maximum 520 nm), acetone (solid line, maximum 510 nm) and propan-2-ol (open circles, maximum 504 nm).

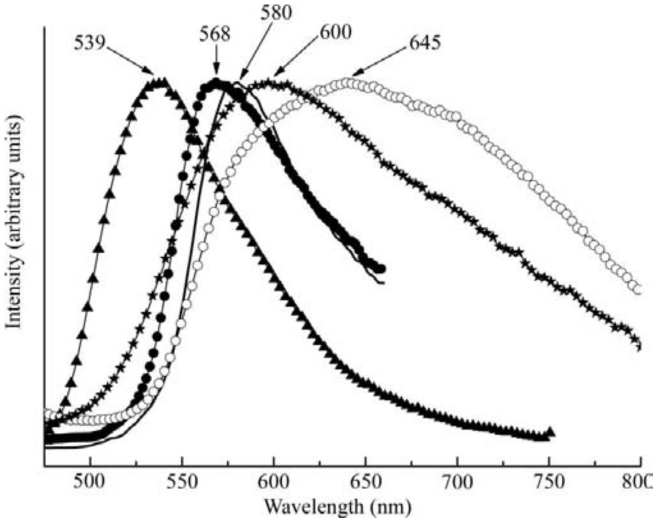

Figure 7
Luminescence spectra of the rubidium salt (triangles, maximum 539 nm, aqueous solution), the rubidium salt (filled circles, maximum 568 nm, solid state), the potassium salt (solid line, maximum 580 nm, solid state), the ammonium salt (stars, maximum 600 nm, solid state) and the sodium salt (open circles, maximum 645 nm, solid state).

The energy emission profiles of the salts containing solvent water molecules (ammonium and sodium) differ (Fig. 7) from those without solvates (potassium and rubidium). As mentioned above, the anion packing motifs for the ammonium and sodium salts are similar but differ from that of the mutually isomorphous potassium and rubidium salts. The nature of these similarities and differences in the crystal structures and emission energy profiles are beyond the scope of this paper and require additional investigation.

In conclusion, there are many factors that affect the luminescence properties of the salts in the solid state, *viz*. hydrogen bonding, the charge on the cation, the π–π interaction details, and so on. Thus, the correlation between structural details and emission energies that we observed can be extended to other salts only with caution.

Experimental

The title salts were obtained by mixing the alkali metal iodide (MI, M = Na and K) in aqueous solution with a suspension of 2,2,3,3-tetracyanocyclopropanecarboxylic acid in propan-2-ol, in a molar ratio of 1:1, or by mixing an RbCl and HI aqueous solution with a suspension of 2,2,3,3-tetracyanocyclopropanecarboxylic acid in propan-2-ol, in a molar ratio of 1:1:1. The reactions were carried out at room temperature, and the water and propan-2-ol v/v ratios were taken as 1:1. Orange powders were separated from the reaction mixtures by filtration and drying. The resulting clear yellow solutions were left aside at 323 K. Upon slow evaporation with heating over a period of 7–10 d, red–orange crystals of the rubidium salt (solvent: water), orange crystals of the potassium salt (solvent: water–propan-2-ol, 1:1 v/v) and orange crystals of the sodium salt (solvent: water–ethanol, 1:1 v/v) had grown.

Salt (I)

Crystal data

$Rb^+\cdot C_8HN_4O_2^-$
M_r = 270.60
Monoclinic, $P2_1/c$
a = 4.2753 (5) Å
b = 9.6013 (9) Å
c = 21.614 (2) Å
β = 95.215 (9)°
V = 883.53 (16) Å^3
Z = 4
Cu $K\alpha$ radiation
μ = 7.62 mm^{-1}
T = 295 (2) K
0.1 × 0.08 × 0.05 mm

Data collection

Enraf–Nonius CAD-4 diffractometr
Absorption correction: ψ scan
(North *et al.*, 1968)
$T_{\min}$ = 0.518, $T_{\max}$ = 0.678
1834 measured reflections
1787 independent reflections
1637 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.041
2 standard reflections
frequency: 60 min
intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.072$
$S = 1.05$
1787 reflections
140 parameters
All H-atom parameters refined
$\Delta\rho_{\max} = 0.49$ e Å^{-3}
$\Delta\rho_{\min} = -0.41$ e Å^{-3}

Table 1
Selected bond lengths (Å) for (I).

Rb—O2^{i}	2.964 (2)	Rb—N3^{iv}	3.099 (3)
Rb—O2	3.001 (2)	Rb—N4^{v}	3.147 (3)
Rb—O1^{ii}	3.020 (2)	Rb—N3	3.189 (3)
Rb—N2^{iii}	3.035 (2)	Rb—N3^{vi}	3.271 (3)
Rb—N4^{iii}	3.075 (3)		

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

Salt (**II**)

Crystal data

$Na^+\cdot C_8HN_4O_2^-\cdot 2H_2O$
$M_r = 244.15$
Triclinic, $P\overline{1}$
$a = 3.6549$ (8) Å
$b = 10.1920$ (12) Å
$c = 14.8401$ (16) Å
$\alpha = 108.849$ (12)°
$\beta = 94.079$ (12)°
$\gamma = 91.58$ (2)°
$V = 521.09$ (14) Å^3
$Z = 2$
Cu $K\alpha$ radiation
$\mu = 1.45$ mm^{-1}
$T = 296$ (2) K
0.04 × 0.01 × 0.01 mm

Data collection

Enraf–Nonius CAD-4 diffractometr
1794 measured reflections
1721 independent reflections
1212 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.077$
2 standard reflections
frequency: 60 min
intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.144$
$S = 1.05$
1721 reflections
178 parameters
All H-atom parameters refined
$\Delta\rho_{\max} = 0.30$ e Å^{-3}
$\Delta\rho_{\min} = -0.24$ e Å^{-3}

Table 2
Selected bond lengths (Å) for (II).

Na1—O3^{i}	2.401 (3)	Na2—O2	2.388 (2)
Na1—O3	2.404 (3)	Na2—O4^{ii}	2.421 (3)
Na1—N4	2.491 (3)	Na2—O4	2.510 (3)
Na1—Na1^{i}	3.6549 (8)		

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

Table 3
Hydrogen-bond geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
O3—H32···N2^{iii}	0.93 (6)	2.03 (6)	2.901 (4)	155 (5)
O3—H31···N3^{iv}	0.85 (5)	2.28 (5)	2.998 (4)	142 (4)
O4—H41···N3^{v}	0.76 (5)	2.21 (5)	2.955 (5)	170 (5)
O4—H42···O1^{vi}	0.87 (6)	2.05 (6)	2.911 (4)	171 (5)
N1—H1···O1^{vi}	0.94 (4)	1.91 (4)	2.827 (3)	165 (3)

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

For the rubidium and sodium salts, the positions of the H atoms were determined from a difference Fourier synthesis and refined freely with the following isotropic displacement parameters: 0.048 (12) Å^2 for the one H atom in the rubidium salt and in the range 0.051 (11)–0.11 (2) Å^2 for the H atoms of the sodium dihydrate salt.

For both compounds, data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2000); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3172). Services for accessing these data are described at the back of the journal.

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