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Luminescent properties of three structures built from 3-cyano-4-dicyanomethylene-5-oxo-4,5-dihydro-1*H*-pyrrol-2-olate and cadmium

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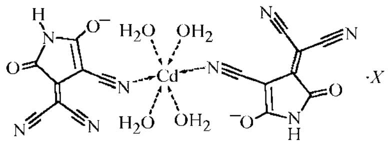
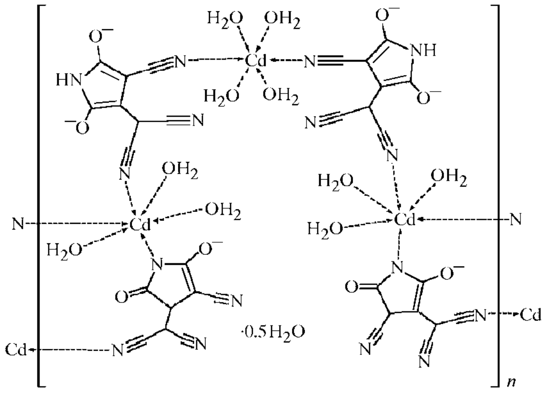
Yellow–orange tetraaquabis(3-cyano-4-dicyanomethylene-5-oxo-4,5-dihydro-1*H*-pyrrol-2-olato-κN^3)cadmium(II) dihydrate, $[Cd(C_8HN_4O_2)_2(H_2O)_4]\cdot 2H_2O$, (I), and yellow tetraaquabis(3-cyano-4-dicyanomethylene-5-oxo-4,5-dihydro-1*H*-pyrrol-2-olato-κN^3)cadmium(II) 1,4-dioxane solvate, $[Cd(C_8HN_4O_2)_2(H_2O)_4]\cdot C_4H_8O_2$, (II), contain centrosymmetric mononuclear Cd^{2+} coordination complex molecules in different conformations. Dark-red poly[[decaaquabis(μ_2-3-cyano-4-dicyanomethylene-5-oxo-4,5-dihydro-1*H*-pyrrol-2-olato-$\kappa^2 N:N'$)bis(μ_2-3-cyano-4-dicyanomethylene-1*H*-pyrrole-2,5-diolato-$\kappa^2 N:N'$)tricadmium] hemihydrate], $[Cd_3(C_8HN_4O_2)_2(C_8N_4O_2)_2(H_2O)_{10}]\cdot 0.5H_2O$, (III), has a polymeric two-dimensional structure, the building block of which includes two cadmium cations (one of them located on an inversion centre), and both singly and doubly charged anions. The cathodoluminescence spectra of the crystals are different and cover the wavelength range from UV to red, with emission peaks at 377 and 620 nm for (III), and at 583 and 580 nm for (I) and (II), respectively.

Comment

Optical, transport and magnetic properties of organic and metal–organic molecular crystals are actively studied nowadays because of the potential applications of these materials as molecular switches, information storage devices, sensors and active components of OLED displays. An important feature of such molecular systems is a pronounced hierarchy of interatomic interactions; bonding within the molecular complex has strong covalent or ionic character, while intermolecular interactions are much weaker. As a result, some physical properties have a local origin (local single molecule characteristics), while others depend on intermolecular contacts of a co-operative nature. An ideal target-oriented and property-directed design of molecular crystals may therefore be subdivided into the synthesis of a molecular unit carrying necessary electronic properties and the packing of molecular units to provide a required collective behaviour and macroscopic properties of interest. Some types of intermolecular contacts were found to be of special importance for conductivity, optics and magnetism (Rochefort *et al.*, 2002; Zheng *et al.*, 2003; Zhao *et al.*, 1999; Inabe *et al.*, 2003; Enoki *et al.*, 2003). In particular, side-by-side contacts (SS, *e.g.* in the case of conjugated polymers) and face-to-face contacts (FF, stacking molecular arrangements) are recognized as important factors in the control of electron transport, optical and magnetic properties of molecular crystals (Epstein, 2000; Matsumoto *et al.*, 2002). Although numerous examples of such contacts can be found among photoconducting, superconducting or magnetically ordered organic polymers, crystals and thin films (Law, 1993, and references therein), control of these properties is often difficult because of the complex schemes of intermolecular interactions. Thus, for most novel materials, this crystal-engineering scenario is still a challenge.



(I) $X = 2H_2O$
(II) $X = C_4H_8O_2$



(III)

Recently, using the organic anion 3-cyano-4-dicyanomethylene-5-oxo-4,5-dihydro-1*H*-pyrrol-2-olate, *A* (Tafeenko *et al.*, 2003, 2005; Tafeenko, Peschar *et al.*, 2004; Tafeenko, Nikolaev *et al.*, 2004), we synthesized a novel type of coordination polymer (Tafeenko & Chernyshev, 2005). Coordination polymers containing cyano-based anions are of great interest because some of them exhibit long-range magnetic ordering (Kurmoo & Kepert, 1998, 1999; Batten *et al.*, 1998). Organic salts based on anion *A* show not only SS and FF types of molecular contacts but also a rich polymorphism, indicating that the molecular unit can be packed in various ways, so giving the opportunity for controlled crystal engineering in relation to optics, conductivity and magnetism. The non-H atoms of the planar anion *A* supply π electrons for π–π (FF) stacking interactions between anions in solids, while the

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dicyanomethylene unit and the nitrile group at the 3-position of the pyrrole cycle, acting as a bridge between metals, enable SS interaction in the polymer. On the basis of the previous structural data and the calculated charge distribution for the atoms of *A*, we can assign the intrinsic intermolecular interactions of the anion as follows: (*a*) every outer (non-H) atom of the anion can be involved in coordination with a metal; (*b*) every outer atom can be involved in hydrogen bonding; (*c*) every cyano group can be involved in intermolecular cyano–cyano interactions; (*d*) every atom of the anion can be involved in π–π stacking interactions. These findings give us a convenient way to compare and describe the novel coordination structures formed with *A*. The objective of our present investigation was to develop novel coordination compounds based on *A* in combination with the Cd^{2+} cation, and to analyse both the coordination modes of the anion and the packing of the molecular unit and relate these to their luminescence properties.

The synthesis of the cadmium coordination compounds was carried out by an exchange reaction of cadmium sulfate and barium 3-cyano-4-dicyanomethylene-5-oxo-4,5-dihydro-1*H*-pyrrol-2-olate. Three types of crystals suitable for X-ray single-crystal investigation were extracted from the precipitate of a slowly evaporated dioxane–water (1:1) solution, namely yellow–orange (I), yellow (II) and dark-red (III). The crystal structures of (I) and (III) contain water solvent molecules, while the solvent molecule in (II) is dioxane.

Both (I) and (II) contain tetraaquabis(3-cyano-4-dicyanomethylene-5-oxo-4,5-dihydro-1*H*-pyrrol-2-olato-κN)cadmium(II) with the Cd^{2+} cation located on an inversion centre. For both samples, the coordination environment consists of four water molecules and two cyano groups (Figs. 1 and 2). The geometric parameters of the coordination mode are similar for the two substances (Tables 1 and 3). The basal angles N—Cd—O and O—Cd—O are in the range 86.31 (9)–93.69 (9)° for (I) and 85.77 (14)–94.23 (14)° for (II), so the octahedral geometry is nearly ideal. There are some deviations in the metal–ligand distances; in (I), the Cd–ligand distances differ somewhat more (Table 1) than in (II) (Table 3). Taking into account that every coordinated water molecule participates in intra- and

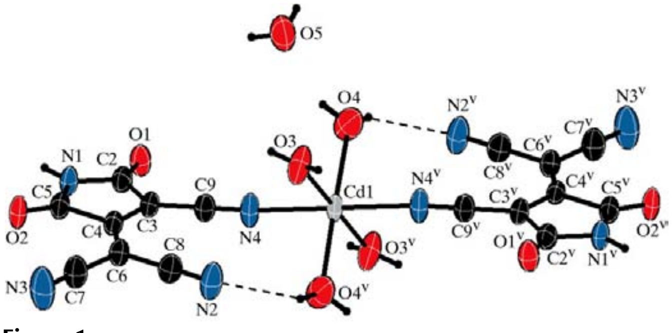

Figure 1
A view of (I), including one of the water solvent molecules, with displacement ellipsoids drawn at the 50% probability level. Intramolecular hydrogen bonds are shown as dashed lines. [Symmetry code: (v) $-x + 1$, $-y + 1$, $-z + 2$.]

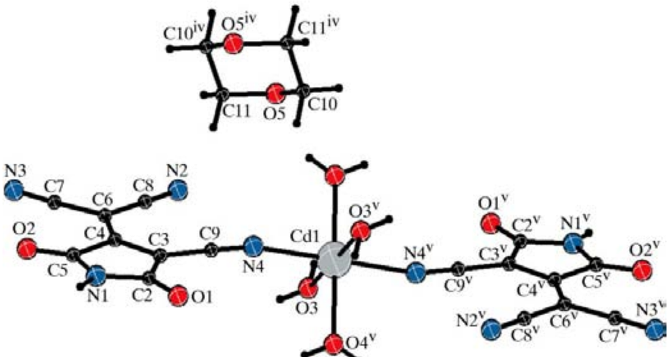

Figure 2
A view of (II), including the dioxane solvent molecule located on an inversion centre, with displacement ellipsoids drawn at the 50% probability level. [Symmetry codes: (iv) $-x$, $-y + 1$, $-z$; (v) $-x + 1$, $-y$, $-z$.]

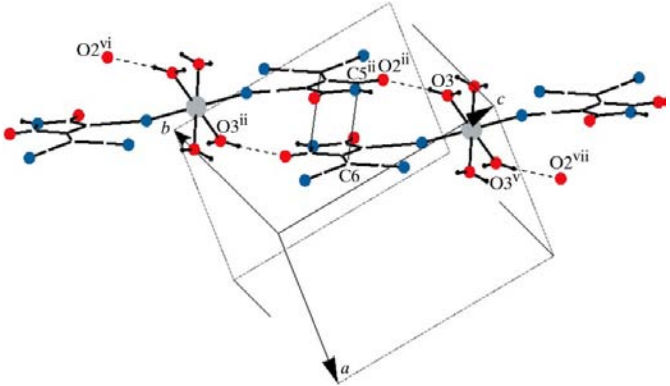

Figure 3
Part of the crystal structure of (I), showing the arrangement of the complexes in a ...*ZZZ*... fashion. [Symmetry codes: (ii) $-x$, $-y + 1$, $-z + 1$; (v) $-x + 1$, $-y + 1$, $-z + 2$; (vi) $-x - 1$, $-y + 1$, $-z$; (vii) $x + 1$, y, $z + 1$.]

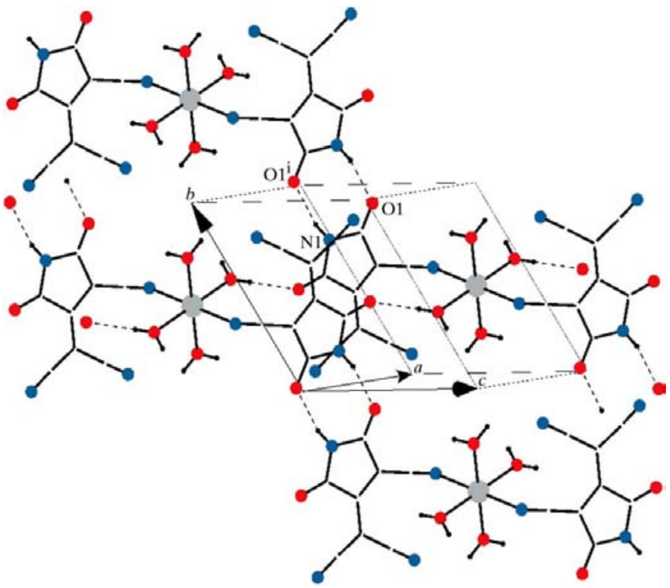

Figure 4
Adjacent blocks in each rod of (I) are connected by centrosymmetric N1—H1···$O1^{i}$ hydrogen bonding, thus forming a layer. [Symmetry code: (i) $-x + 1$, $-y + 2$, $-z + 1$.]

intermolecular hydrogen bonding, it is possible that the minor changes in pure octahedral parameters could be considered a consequence of a packing effect.

Although anion *A* is inflexible, its coordination through the cyano group to the metal may lead to different conformations, as is the case in (I) and (II); the Cd1—N4—C9—C3 torsion angles differ by 61 (1)°. As a result, the shortest intramolecular distances between anions *A* and the coordinated water molecules are substantially different in (I) and (II). We find an intramolecular hydrogen bond (O4—H41···N2^{v}) only in (I) (see Fig. 1 and Table 2). The relevant distances in (II) are 4.268 (5) (O4···N2) and 4.192 (6) Å (O3···N2) (Fig. 2).

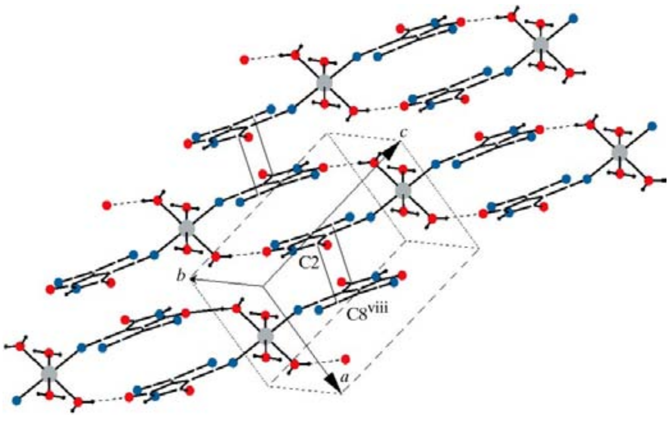

Figure 5
A view of (I), showing how π–π stacking interactions between rods link adjacent layers. The shortest distances between atoms which reflect this π–π interaction are shown as thin lines. [Symmetry code: (viii) $-x + 1, -y + 1, -z + 1$.]

As the packing motifs in (I) and (II) are similar, only packing figures for (I) are presented. Molecules in both (I) and (II) are involved in hydrogen bonding (symmetry codes and other parameters are given in Tables 2 and 4) using mainly two types of hydrogen bonds. The hydrogen bonds O3—H31···O2^{ii} in (I) or O3—H31···O2^{iii} in (II) are complementary to the π–π stacking interactions between anions, and the $[Cd^{2+}(A^{-})_2(H_2O)_4]$ molecules are arranged in a ...*ZZZ*... fashion (Tafeenko & Chernyshev, 2005); thus, infinite $[Cd^{2+}(A^{-})_2(H_2O)_4]_n$ rods (Fig. 3) are formed. Neighbouring rods are linked by centrosymmetric N1—H1···O1^{i} hydrogen bonds resulting in the formation of an infinite layer (Fig. 4). π–π stacking interactions between rods (Fig. 5) and hydrogen bonding through solvent molecules complete the three-dimensional crystal structure. The distances between the mean-square planes through atoms of adjacent anions in (I), representing the π–π stacking interaction, are 3.277 (3) Å (Figs. 3 and 5), while in (II) they differ, *viz.* 3.106 (7) Å between anions of adjacent rods and 3.349 (7) Å between anions in the rods.

In (III), the pyrrole H atom of the anion can be replaced by a metal atom, giving the polymer poly[[decaaquabis(μ_2-3-cyano-4-dicyanomethylene-5-oxo-4,5-dihydro-1*H*-pyrrol-2-olato-κ^2N:N')bis(μ_2-3-cyano-4-dicyanomethylene-3*H*-pyrrole-2,5-diolato-κ^2N:N')tricadmium] 0.5-hydrate] (Fig. 6). This structure shows both novel properties of the anion in question and a novel type of polymeric crystal structure where simultaneously singly and doubly negatively charged anions are present. The polymeric undulated layer of (III), as shown in Fig. 7, can be described as follows: the chains consist of Cd2-based $[Cd^{2+}(A^{2-})(H_2O)_3]$ building blocks that are linked

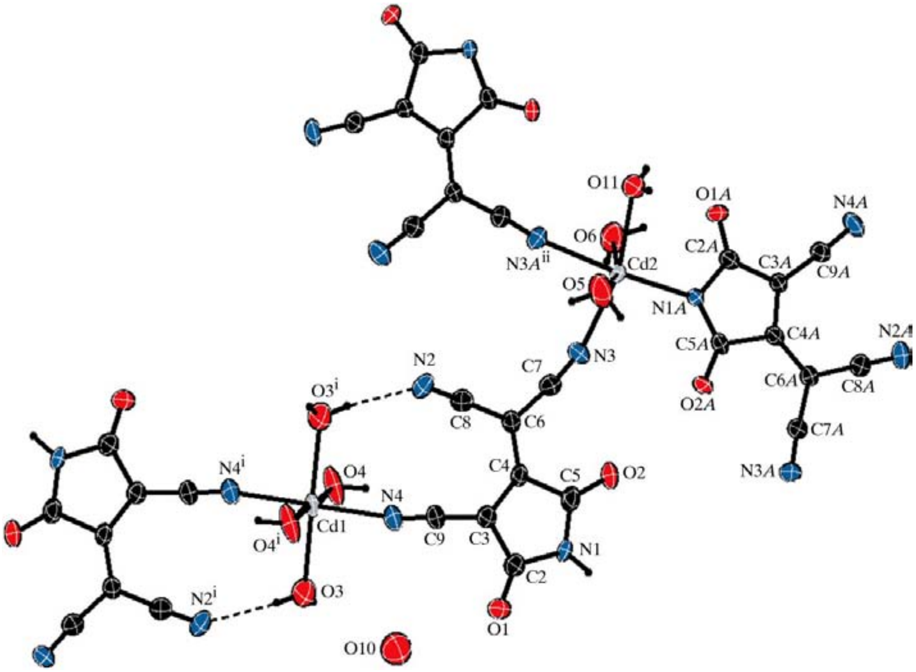

Figure 6
A view of (III), including the water solvent molecule (O10, occupancy factor 0.25) located near a twofold axis, with displacement ellipsoids drawn at the 50% probability level. Atom Cd1 is located on an inversion centre. Intramolecular hydrogen bonds are shown as dashed lines. [Symmetry codes: (i) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z$; (ii) $x - \frac{1}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$.]

head-to-tail by A^{2-} ligands through the pyrrole N atom (N1*A*) and the nitrile N atom (N3*A*$^{\rm ii}$) (Figs. 6 and 7) of the dicyanomethylene unit. Cd1-based [$\rm Cd^{2+}(A^-)_2(H_2O)_4$] building blocks crosslink neighbouring chains through coordination of the cadmium cation in the chain (Cd2) by atom N3 of the monovalent anion, so that the octahedral environment of atom Cd2 in the chain is completed. Hydrogen bonds involving coordinated and uncoordinated water molecules complement the π–π stacking interactions between the anions (Fig. 8), linking adjacent layers into a continuous framework (Table 6).

Atom Cd1 is located on an inversion centre and is coordinated by four water molecules and two A^- ligands, displaying ideally octahedral geometry, which is similar to that found in (I) (see Table 5). All O—Cd1—O and O—Cd1—N angles lie in the range 88.33 (17)–91.67 (17)°. As in (I), an intramolecular O3—H3···N2$^{\rm i}$ hydrogen bond (Fig. 6 and Table 6) occurs. By contrast, atom Cd2 has a distorted octahedral coordination, being bonded to three water molecules and atoms N3, N3*A*$^{\rm ii}$ and N1*A* (symmetry code as in Table 5). The octahedral distortion results primarily from the coordination through atom N1*A*, the N1*A*—Cd2 distance being the shortest among all Cd–ligand distances in the three crystal structures (see Table 5). Moreover, all the equatorial atoms are bent towards apical atom N3*A*$^{\rm ii}$, with all the (O,N)—Cd2—N3*A*$^{\rm ii}$ angles smaller than 90° (Fig. 6). The shortest Cd1···Cd2 distance between cations is 5.548 (1) Å.

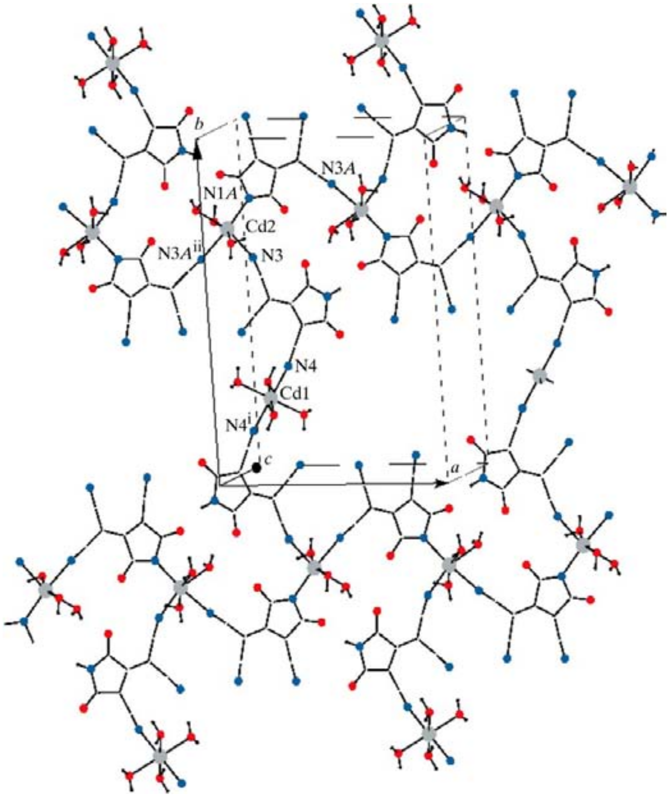

Figure 7
Part of the crystal structure of (III), showing the chains running along the *a* axis and the resulting undulated layers. [Symmetry codes: (i) $-x+\frac{1}{2}$, $-y+\frac{1}{2}$, $-z$; (ii) $x-\frac{1}{2}$, $-y+\frac{3}{2}$, $z-\frac{1}{2}$.]

The cathodoluminescence (CL) spectra of (I) and (II) are similar, so only the spectra of (I) and (III) are shown in Fig. 9. The CL spectrum of (I) shows a broad peak at 583 nm. The CL spectrum of (III) differs drastically and exhibits two emission bands with maxima at 377 and 620 nm. The UV emission of 377 nm may be attributed to a doubly charged anion, while the emission peaks at 583 and 620 nm can be related to the charge recombination through the singly charged anion. To be sure that the luminescence originates from the anions, we further measured the emission spectra of the ammonium salt of *A*. We chose the ammonium salt because of the common features (hydrogen-bonding dimers and π–π stacking motifs) of the packing of the anions in (I) and in the ammonium salt (Tafeenko, Peschar *et al.*, 2005). Figs. 9 and 10 illustrate that the luminescence spectra of the ammonium salt and (I) are similar, and thus the key role of the anions as the origin of the

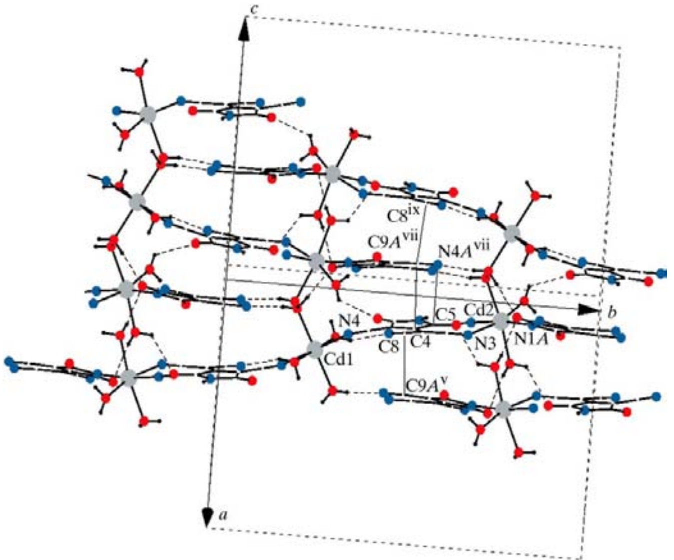

Figure 8
The anions of adjacent layers in (III) are connected by π–π interactions to form the three-dimensional structure. The shortest distances between atoms which reflect these π–π interactions are shown as thin lines. The hydrogen bonds are shown as dashed lines. [Symmetry codes: (v) $-x+\frac{1}{2}$, $-y+\frac{3}{2}$, $-z$; (vii) $-x+\frac{1}{2}$, $y-\frac{1}{2}$, $-z+\frac{1}{2}$; (ix) x, $-y+1$, $z+\frac{1}{2}$.]

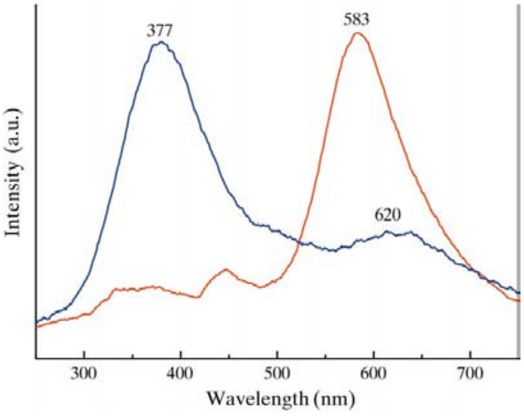

Figure 9
The CL spectra of (I), with a peak at 583 nm, and (III), with peaks at 377 and 620 nm.

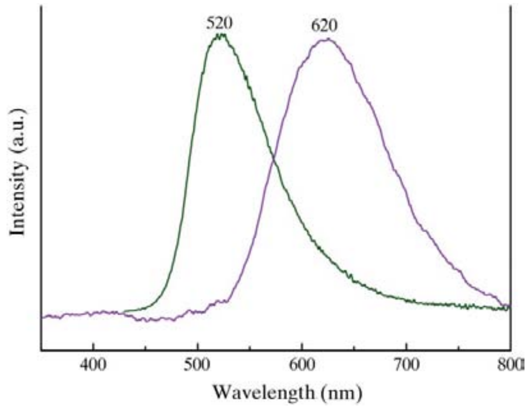

Figure 10
The CL spectrum of the ammonium salt in the solid state, with a peak at 620 nm, and the photoluminescence spectrum of its water solution, with a peak at 520 nm.

luminescence of the salts in question is proved, *i.e.* we are able to exclude the influence of the metal on the luminescence.

In conclusion, we emphasize that: (*a*) the arrangement of the octahedral *A*-containing complexes in a ...*ZZZ*... fashion (Tafeenko & Chernyshev, 2005) is a major factor in the formation of their crystal structures; (*b*) the luminescence of compounds based on *A* covers the wavelength range from UV to red. Tuning of the emission photon energy can be carried out on the basis of controllable intermolecular interactions of a co-operative nature. We illustrate this by comparing the luminescence spectrum of the ammonium salt in solution and the CL spectrum of the solid (Fig. 10). The maximum of the emission band of the ammonium salt in the solid is at 620 nm, while in water it is at 520 nm, implying that the intermolecular interaction in the crystal structure leads to a spectral shift of about 100 nm.

Experimental

The syntheses of the cadmium salts were carried out by slow addition of a cadmium sulfate solution (1.5 mmol of $CdSO_4$ in 10 ml of a 1:1 mixture of dioxane and water) to a 10 ml solution of barium 3-cyano-4-(dicyanomethylene)-5-oxo-4,5-dihydro-1*H*-pyrrol-2-olate (1.1 mmol of salt in 10 ml of 1:1 dioxane–water). A white precipitate formed immediately and was filtered off after 3 h. The clear yellow solution was left aside for crystallization at room temperature. Over a period of four weeks, yellow and then red crystals were formed. The crystals were filtered off, washed with a small portion of cool water and dried in air. Red, orange and yellow crystals suitable for X-ray investigation were separated mechanically. (See the supplementary materials for the CL and photoluminescence spectral analysis details.)

Compound (I)

Crystal data

$[Cd(C_8HN_4O_2)_2(H_2O)_4]\cdot 2H_2O$
$M_r = 590.76$
Triclinic, $P\overline{1}$
$a = 6.987$ (2) Å
$b = 8.645$ (2) Å
$c = 10.567$ (3) Å
$\alpha = 105.48$ (2)°
$\beta = 97.08$ (2)°
$\gamma = 110.28$ (3)°
$V = 560.3$ (3) Å^3
$Z = 1$
Mo $K\alpha$ radiation
$\mu = 1.05$ mm^{-1}
$T = 295$ (2) K
$0.10 \times 0.10 \times 0.05$ mm

Data collection

Enraf–Nonius CAD-4 diffractometr
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.903$, $T_{max} = 0.950$
2823 measured reflections
2693 independent reflections
2503 reflections with $I > 2\sigma(I)$
$R_{int} = 0.012$
2 standard reflections
frequency: 120 min
intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.071$
$S = 1.05$
2693 reflections
166 parameters
9 restraints
H-atom parameters constrained
$\Delta\rho_{max} = 0.42$ e Å^{-3}
$\Delta\rho_{min} = -0.39$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

Cd1—O4	2.242 (2)	Cd1—N4	2.327 (2)
Cd1—O3	2.264 (2)		
O4—Cd1—O3	89.47 (10)	O3—Cd1—N4	86.31 (9)
O4—Cd1—N4	90.89 (9)		

Table 2
Hydrogen-bond geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1^{i}	0.86	2.03	2.870 (3)	164
O4—H4···O5	0.82	2.01	2.773 (4)	155
O3—H31···O2^{ii}	0.79	2.05	2.837 (3)	175
O5—H51···N3^{ii}	0.83	2.08	2.874 (4)	161
O3—H3···O5^{iii}	0.82	2.17	2.825 (4)	137
O5—H5···O1^{iv}	0.83	2.34	2.949 (3)	131
O4—H41···N2^{v}	0.87	2.33	2.986 (3)	132

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

Compound (II)

Crystal data

$[Cd(C_8HN_4O_2)_2(H_2O)_4]\cdot C_4H_8O_2$
$M_r = 642.83$
Triclinic, $P\overline{1}$
$a = 6.9511$ (10) Å
$b = 8.4052$ (12) Å
$c = 11.3293$ (16) Å
$\alpha = 84.61$ (2)°
$\beta = 72.523$ (10)°
$\gamma = 88.340$ (10)°
$V = 628.57$ (16) Å^3
$Z = 1$
Mo $K\alpha$ radiation
$\mu = 0.94$ mm^{-1}
$T = 295$ (2) K
$0.12 \times 0.10 \times 0.06$ mm

Data collection

Enraf–Nonius CAD-4 diffractometr
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.912$, $T_{max} = 0.955$
3173 measured reflections
3022 independent reflections
2239 reflections with $> \sigma(I)$
$R_{int} = 0.018$
2 standard reflections
frequency: 120 min
intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.114$
$S = 0.98$
3022 reflections
178 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.61$ e Å^{-3}
$\Delta\rho_{min} = -0.59$ e Å^{-3}

Table 3
Selected geometric parameters (Å, °) for (II).

Cd1—O4	2.269 (3)	Cd1—O3	2.300 (4)
Cd1—N4	2.276 (4)		
O4—Cd1—N4	89.99 (13)	N4—Cd1—O3	92.66 (14)
O4—Cd1—O3	85.77 (14)		

Table 4
Hydrogen-bond geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
O4—H41···O5	0.81	2.12	2.831 (5)	145
N1—H1···O1$^{\rm i}$	0.86	1.98	2.831 (5)	172
O3—H3···O5$^{\rm ii}$	0.82	2.18	2.993 (6)	169
O4—H4···N2$^{\rm ii}$	0.82	2.18	2.893 (5)	145
O3—H31···O2$^{\rm iii}$	0.81	2.21	2.940 (5)	151

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

Compound (III)

Crystal data

$[\mathrm{Cd_3(C_8HN_4O_2)_2(C_8N_4O_2)_2(H_2O)_{10}]\cdot 0.5H_2O}$
$M_r = 1263.89$
Monoclinic, $C2/c$
$a = 18.3348\ (12)$ Å
$b = 19.9640\ (15)$ Å
$c = 13.5231\ (11)$ Å
$\beta = 119.77\ (2)^\circ$
$V = 4296.7\ (10)$ Å^3
$Z = 4$
Cu $K\alpha$ radiation
$\mu = 12.64$ mm^{-1}
$T = 295\ (2)$ K
0.20 × 0.15 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 diffractometr
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\rm min} = 0.150$, $T_{\rm max} = 0.385$ (expected range = 0.110–0.282)
4312 measured reflections
4123 independent reflections
3473 reflections with $> \sigma(I)$
$R_{\rm int} = 0.025$
2 standard reflections frequency: 120 min intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.118$
$S = 1.02$
4123 reflections
324 parameters
9 restraints
H-atom parameters constrained
$\Delta\rho_{\rm max} = 0.76$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.98$ e Å^{-3}

Table 5
Selected geometric parameters (Å, °) for (III).

Cd1—O4	2.265 (5)	Cd2—N3$A^{\rm ii}$	2.338 (5)
Cd1—N4	2.296 (5)	Cd2—O6	2.343 (5)
Cd1—O3$^{\rm i}$	2.296 (5)	Cd2—N3	2.347 (5)
Cd2—N1A	2.214 (4)	Cd2—O11	2.384 (4)
Cd2—O5	2.306 (5)		
O4—Cd1—N4	91.67 (17)	N1A—Cd2—N3	98.32 (16)
O4—Cd1—O3	91.0 (2)	O5—Cd2—N3	87.18 (19)
N4—Cd1—O3	90.40 (18)	N3$A^{\rm ii}$—Cd2—N3	85.12 (17)
N1A—Cd2—O5	106.30 (17)	O6—Cd2—N3	95.70 (19)
N1A—Cd2—N3$A^{\rm ii}$	171.08 (17)	N1A—Cd2—O11	98.23 (14)
O5—Cd2—N3$A^{\rm ii}$	82.02 (19)	O5—Cd2—O11	82.23 (18)
N1A—Cd2—O6	90.77 (16)	N3$A^{\rm ii}$—Cd2—O11	79.43 (16)
O5—Cd2—O6	162.13 (17)	O6—Cd2—O11	90.28 (18)
N3$A^{\rm ii}$—Cd2—O6	80.67 (18)	N3—Cd2—O11	162.31 (16)

Symmetry codes: (i) $-x+\frac{1}{2}, -y+\frac{1}{2}, -z$; (ii) $x-\frac{1}{2}, -y+\frac{3}{2}, z-\frac{1}{2}$.

Table 6
Hydrogen-bond geometry (Å, °) for (III).

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3···N2$^{\rm i}$	0.82	2.11	2.889 (7)	158
N1—H1···O1$A^{\rm iii}$	0.86	1.91	2.730 (5)	160
O11—H11···O1$^{\rm iv}$	0.82	2.29	2.851 (6)	127
O11—H111···O2$^{\rm ii}$	0.82	2.38	3.127 (6)	153
O6—H61···O2$^{\rm v}$	0.90	2.28	2.922 (6)	129
O4—H41···N4$A^{\rm v}$	0.88	1.94	2.749 (6)	153
O4—H4···O2$A^{\rm vi}$	0.82	1.98	2.779 (6)	166
O5—H5···N2$A^{\rm vii}$	0.82	2.06	2.871 (7)	168
O3—H31···O11$^{\rm viii}$	0.88	2.34	3.149 (7)	154
O5—H51···O4$^{\rm ix}$	0.88	2.13	2.980 (8)	162
O6—H6···O2$A^{\rm v}$	0.82	2.15	2.922 (7)	158

Symmetry codes: (i) $-x+\frac{1}{2}, -y+\frac{1}{2}, -z$; (ii) $x-\frac{1}{2}, -y+\frac{3}{2}, z-\frac{1}{2}$; (iii) $x+\frac{1}{2}, -y+\frac{3}{2}, z+\frac{1}{2}$; (iv) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (v) $-x+\frac{1}{2}, -y+\frac{3}{2}, -z$; (vi) $x, -y+1, z-\frac{1}{2}$; (vii) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (viii) $x+\frac{1}{2}, y-\frac{1}{2}, z$; (ix) $x, -y+1, z+\frac{1}{2}$.

For (I), (II) and (III), the positions of the H atoms were determined from a difference Fourier map, and these atoms were allowed to ride on their parent atoms, with $U_{\rm iso}$(H) values set at 1.2 (for nitrogen) and 1.5 (for oxygen) times $U_{\rm eq}$ of the attached atoms. The water solvent molecule in (III) is disordered near to a twofold axis. The displacement parameter of this water molecule (O10) was fixed at 0.067 Å^2; the final value of the site occupancy of (O10) was 0.25 for the lowest agreement factor.

For all 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, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); 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: GA3063). Services for accessing these data are described at the back of the journal.

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