data reports

Poly[bis(trimethylammonium) [hexa-μ-cyanido-cadmium(II)dicopper(I)]]

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The title compound, $\{(C_3H_{10}N)_2[CdCu_2(CN)_6]\}_n$, has been synthesized as an alternative to the high-emitting complexes containing more expensive metals. The CN^- ligands make linkages between the Cu^I and Cd^{II} ions to form the coordination polymer, $[CdCu_2(CN)_6]_n^{2-}$, which is a three-dimensional framework classified as pyrite net (**pyr**). The net has a void space for accommodating a trimethylammonium ion located on a threefold rotation axis. The Cd^{II} ion lies on a special position with site symmetry $\bar{3}$ and is octahedrally coordinated by six N atoms. The Cu^I ion is located on a threefold rotation axis and has a trigonal-planar coordination geometry formed by three C atoms. In the three-dimensional net, two Cu^I ions are arranged closely $[Cu\cdots Cu = 3.9095\,(5)\,Å]$, but the distance is not short enough to suggest a Cu^I–Cu^I interaction. The crystal studied was a merohedral twin (twin operation $2_{[101]}$), the refined component ratio being 0.9202 (7):0.0798 (7). A powder of the title compound shows strong luminescence with an emission maximum at 509 nm and a quantum yield of 98% at room temperature.

3D view
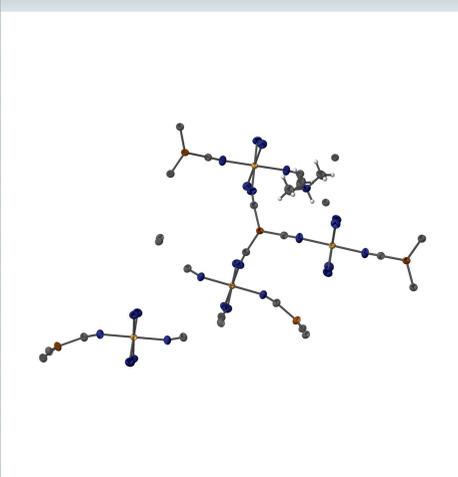
Chemical scheme
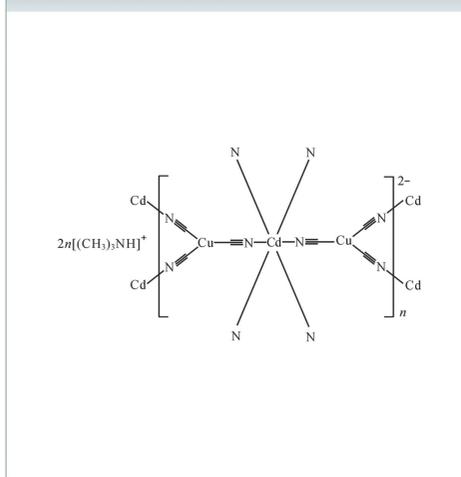
Structure description

The title compound, a coordination polymer formed by Cu^I and Cd^{II} ions and bridging CN^- ligands, has been synthesized as an alternative to the high-emitting complexes containing more expensive metals. Combinations of Cu^I, CN^- and other building ligands have previously been used for such purposes (Lim *et al.*, 2008; Dembo *et al.*, 2010). The objective of the present work was to build a more robust and lower energy loss coordination polymer by adding Cd^{II} ions. These ions are well known as excellent building blocks for three-dimensional net structures (Iwamoto, 1996), and exhibit no emissive *d*–*d* metal-centred levels (Barbieri *et al.*, 2008). A powder of the title compound showed
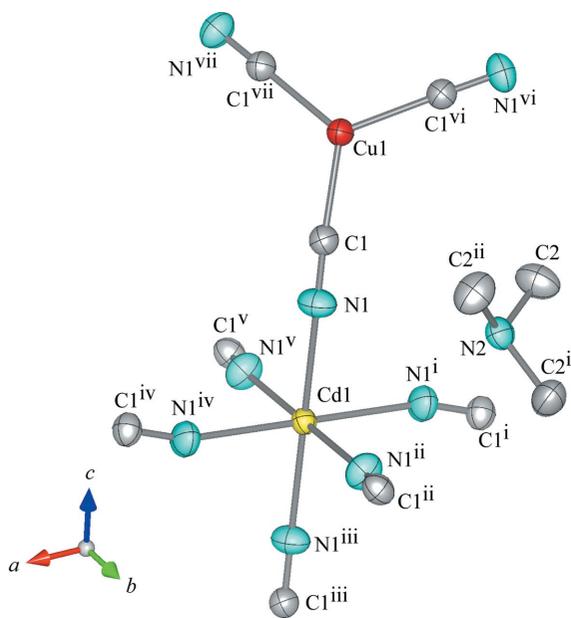
Figure 1
The coordination forms of the Cd^{II} and Cu^{I} ions and the structure of the trimethylammonium ion in the title compound. All displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity. [Symmetry codes: (i) $-z + \frac{1}{2}, -x + 1, y - \frac{1}{2}$; (ii) $-y + 1, z + \frac{1}{2}, -x + \frac{1}{2}$; (iii) $-x + 1, -y + 1, -z$; (iv) $z + \frac{1}{2}, x, -y + \frac{1}{2}$; (v) $y, -z + \frac{1}{2}, x - \frac{1}{2}$; (vi) z, x, y; (vii) y, z, x.]

luminescence with an emission maximum at 509 nm and a quantum yield of 98% at room temperature.

The Cu^{I} ion resides on a threefold rotation axis and has a trigonal-planar coordination geometry by the C atoms of three CN^{-} ligands. The N-terminals of the CN^{-} ligands are linked to the Cd^{II} ions, which are located on special positions with $\bar{3}$ site symmetry (Fig. 1). The orientation of the bridging CN^{-} ions
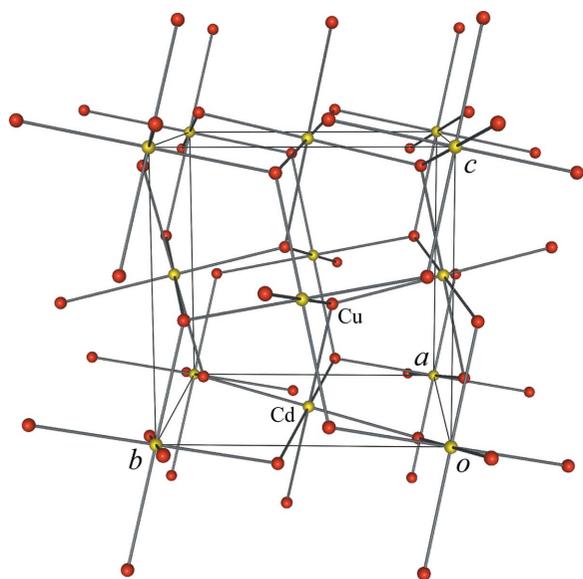
Figure 2
Pyrite net (**pyr**) of the coordination polymer $[CdCu_2(CN)_6]_n^{2-}$. The CN^{-} ligands linking the Cd^{II} (octahedral coordination sphere) and the Cu^{I} (trigonal-planar coordination sphere) ions are represented as solid lines.
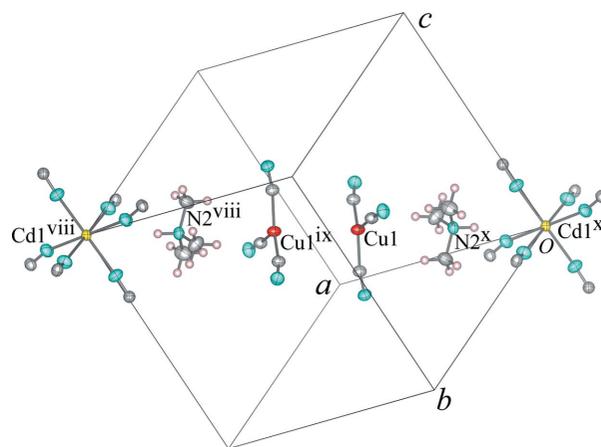
Figure 3
An arrangement of the Cd^{II} (octahedral coordination sphere), Cu^{I} (trigonal-planar coordination sphere) and (CH$_3$)$_3$NH$^+$ ions on the threefold rotation axis running along the diagonal line of the unit cell. The distance between Cu1 and Cu1^{ix} is 3.9095 (5) Å. [Symmetry codes: (viii) $x + \frac{1}{2}, -y + \frac{3}{2}, 1 - z$; (ix) $1 - x, 1 - y, 1 - z$; (x) $x - \frac{1}{2}, -y + \frac{1}{2}, -z$; (xi) $x - \frac{1}{2}, -y + \frac{1}{2}, -z$.]

was confirmed by ^{113}Cd CP/MAS NMR spectra, which showed a single peak at a chemical shift of 191 p.p.m. [referenced to an external Cd(NO$_3$)$_2$·4H$_2$O standard]. This chemical shift indicates that each Cd^{II} ion is octahedrally coordinated by six N atoms (Nishikiori *et al.*, 1990). The Cu^{I}—CN—Cd^{II} linkages form an infinite $[CdCu_2(CN)_6]_n^{2-}$ three-dimensional net. The topology of this net is characterized as **pyr** (pyrite net; Fig. 2),

Table 1
Experimental details.

Crystal data	
Chemical formula	(C$_3$H$_{10}$N)$_2$[CdCu$_2$(CN)$_6$]
M_r	515.87
Crystal system, space group	Cubic, $Pa\bar{3}$
Temperature (K)	296
a (Å)	12.3775 (9)
V (Å^3)	1896.3 (4)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	3.34
Crystal size (mm)	0.32 × 0.29 × 0.22
Data collection	
Diffractometer	Bruker APEXII
Absorption correction	Multi-scan (*SADABS*; Bruker, 2012)
T_{min}, T_{max}	0.627, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	11150, 861, 772
R_{int}	0.025
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.677
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.017, 0.044, 1.11
No. of reflections	861
No. of parameters	38
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.28, −0.28

Computer programs: *APEX2* and *SAINT* (Bruker, 2012), *SHELXS97* (Sheldrick 2008), *SHELXL2017* (Sheldrick, 2015), *VESTA 3* (Momma & Izumi, 2011) and *publCIF* (Westrip, 2010).

the same as that of MOF-150 (Chae *et al.*, 2003). The two closest $Cu(CN)_3$ units, which reside on the same threefold rotation axis, are stacked in a staggered conformation with an inversion centre at their mid point (Fig. 3). The distance between the two Cu^I ions [3.9095 (5) Å] precludes a Cu^I–Cu^I interaction, the contribution of which to luminescence behaviour has previously been discussed (Nishikawa *et al.*, 2016). The $(CH_3)_3NH^+$ ions that balance the negative charges of the three-dimensional polymer are trapped in the voids of the pyrite net. The principal axis of the $(CH_3)_3NH^+$ ion coincides with the threefold rotation axis on which the Cu^I and Cd^{II} ions reside. The lone H atom of the $(CH_3)_3NH^+$ ion is oriented towards the Cd^{II} ion (Fig. 3).

Synthesis and crystallization

The title compound was prepared from an aqueous solution containing $Cd(CN)_2$, CuCN, NaCN and $(CH_3)_3NHCl$. Into 20 ml of water $Cd(CN)_2$ (0.33 g, 2 mmol), CuCN (0.18 g, 2 mmol) and NaCN (0.40 g, 8.2 mmol) were added. The mixture was warmed with stirring until it turned to a clear solution. Then, $(CH_3)_3NHCl$ (0.19 g, 2 mmol) was dissolved into the solution. After keeping the solution at 278 K for a week, colourless crystals of the title compound were obtained. Analysis calculated for $C_{12}H_{20}CdCu_2N_8$: C 27.94, H 3.91, N 21.72%; found: C 27.85, H 3.98, N 21.87%.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. In the final stage, the refinement was carried out assuming merohedral twinning, as suggested by the *PLATON* program (Spek, 2015), with the twin operation $2_{[101]}$, and the final BASF parameter was 0.0798 (7).

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full crystallographic data

Poly[bis(trimethylammonium) [hexa-*μ*-cyanido-cadmium(II)dicopper(I)]]

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Poly[bis[(trimethylammonium) [hexa-*μ*-cyanido-cadmium(II)dicopper(I)]

Crystal data

$(C_3H_{10}N)_2[CdCu_2(CN)_6]$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$M_r = 515.87$	Cell parameters from 5459 reflections
Cubic, $Pa\overline{3}$	$\theta = 2.9$–28.5°
$a = 12.3775$ (9) Å	$\mu = 3.34$ mm^{-1}
$V = 1896.3$ (4) Å^3	$T = 296$ K
$Z = 4$	Block, colourless
$F(000) = 1016$	$0.32 \times 0.29 \times 0.22$ mm
$D_x = 1.807$ Mg m^{-3}	

Data collection

Bruker APEXII diffractometer	11150 measured reflections
Radiation source: fine-focus sealed tube	861 independent reflections
Graphite monochromator	772 reflections with $I > 2\sigma(I)$
Detector resolution: 8.3333 pixels mm^{-1}	$R_{int} = 0.025$
phi and ω scans	$\theta_{max} = 28.8°$, $\theta_{min} = 1.7°$
Absorption correction: multi-scan (SADABS; Bruker, 2012)	$h = -16 \rightarrow 11$
	$k = -14 \rightarrow 16$
$T_{min} = 0.627$, $T_{max} = 0.746$	$l = -15 \rightarrow 16$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.017$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.044$	
$S = 1.11$	H-atom parameters constrained
861 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0208P)^2 + 0.6318P]$ where $P = (F_o^2 + 2F_c^2)/3$
38 parameters	
0 restraints	$(\Delta/\sigma)_{max} < 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.28$ e Å^{-3}
	$\Delta\rho_{min} = -0.28$ e Å^{-3}

Special details

Geometry. Bond distances, angles etc. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell esds are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refined as a 2-component twin.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cd1	0.500000	0.500000	0.000000	0.02365 (9)
Cu1	0.40882 (2)	0.40882 (2)	0.40882 (2)	0.03148 (11)
N1	0.48328 (15)	0.49244 (15)	0.18799 (14)	0.0413 (4)
C1	0.46209 (16)	0.46692 (16)	0.27362 (15)	0.0335 (4)
N2	0.29859 (12)	0.70141 (12)	0.20141 (12)	0.0338 (6)
H2	0.344303	0.655696	0.155697	0.041*
C2	0.20128 (19)	0.6377 (2)	0.23072 (19)	0.0521 (6)
H2A	0.222902	0.572912	0.267472	0.078*
H2B	0.162203	0.619101	0.166360	0.078*
H2C	0.155818	0.679893	0.277288	0.078*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cd1	0.02365 (9)	0.02365 (9)	0.02365 (9)	0.00096 (6)	0.00096 (6)	−0.00096 (6)
Cu1	0.03148 (11)	0.03148 (11)	0.03148 (11)	0.00670 (10)	0.00670 (10)	0.00670 (10)
N1	0.0470 (10)	0.0483 (11)	0.0286 (8)	−0.0062 (8)	0.0020 (7)	0.0031 (7)
C1	0.0340 (9)	0.0340 (9)	0.0324 (9)	0.0042 (8)	0.0033 (8)	0.0028 (7)
N2	0.0338 (6)	0.0338 (6)	0.0338 (6)	0.0038 (6)	0.0038 (6)	−0.0038 (6)
C2	0.0514 (13)	0.0599 (14)	0.0450 (12)	−0.0161 (11)	0.0071 (10)	−0.0003 (11)

Geometric parameters (Å, º)

Cd1—N1	2.3379 (17)	N1—C1	1.137 (3)
Cd1—N1[i]	2.3379 (17)	N2—C2	1.485 (3)
Cd1—N1[ii]	2.3379 (17)	N2—C2[i]	1.485 (3)
Cd1—N1[iii]	2.3379 (17)	N2—C2[ii]	1.485 (3)
Cd1—N1[iv]	2.3379 (17)	N2—H2	0.9800
Cd1—N1[v]	2.3379 (17)	C2—H2A	0.9600
Cu1—C1	1.9371 (19)	C2—H2B	0.9600
Cu1—C1[vi]	1.9371 (19)	C2—H2C	0.9600
Cu1—C1[vii]	1.9371 (19)		
N1—Cd1—N1[i]	87.44 (6)	C1—Cu1—C1[vii]	119.24 (8)
N1—Cd1—N1[ii]	87.44 (6)	C1[vi]—Cu1—C1[vii]	119.24 (8)
N1—Cd1—N1[iii]	180.00	Cd1—N1—C1	163.66 (17)
N1—Cd1—N1[iv]	92.56 (6)	Cu1—C1—N1	170.85 (18)
N1—Cd1—N1[v]	92.56 (6)	C2—N2—C2[i]	111.25 (16)
N1[i]—Cd1—N1[ii]	87.44 (6)	C2—N2—C2[ii]	111.25 (16)
N1[i]—Cd1—N1[iii]	92.56 (6)	C2[i]—N2—C2[ii]	111.25 (16)
N1[i]—Cd1—N1[iv]	180.00	C2—N2—H2	108.00
N1[i]—Cd1—N1[v]	92.56 (6)	C2[i]—N2—H2	108.00
N1[ii]—Cd1—N1[iii]	92.56 (6)	C2[ii]—N2—H2	108.00
N1[ii]—Cd1—N1[iv]	92.56 (6)	N2—C2—H2A	109.00
N1[ii]—Cd1—N1[v]	180.00	N2—C2—H2B	109.00

N1^{iii}—Cd1—N1^{iv}	87.44 (6)	N2—C2—H2C	109.00
N1^{iii}—Cd1—N1^{v}	87.44 (6)	H2A—C2—H2B	109.00
N1^{iv}—Cd1—N1^{v}	87.44 (6)	H2A—C2—H2C	109.00
C1—Cu1—C1^{vi}	119.24 (8)	H2B—C2—H2C	109.00

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