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Bis[bis(3,5-dimethylpyrazol-1-yl)methane]bis(isothiocyanato)cadmium(II) and *catena*-poly[[di-μ-dicyanamidato-bis{[bis(3,5-dimethylpyrazol-1yl)methane]cadmium(II)}]-di-μ-dicyanamidato]

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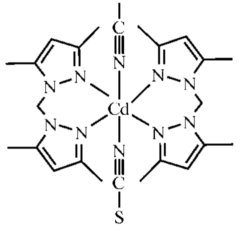
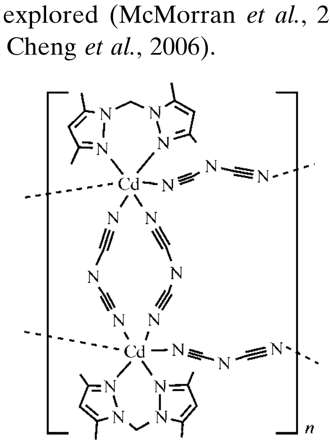
The Cd atom in bis[bis(3,5-dimethylpyrazol-1-yl)methane]-bis(isothiocyanato)cadmium(II), $[Cd(NCS)_2(C_{11}H_{16}N_4)_2]$, is octahedrally coordinated by four N atoms from two bis(3,5-dimethylpyrazolyl)methane (dmpzm) ligands and two isothiocyanate ligands. The molecule has a crystallographic center of symmetry located at the Cd atom. There are two intramolecular C—H$\cdots$N interactions, each of which is formed between the methylene group of a dmpzm ligand and the N atom of an isothiocyanate ligand. On the other hand, in *catena*-poly[[di-μ-dicyanamidato-bis{[bis(3,5-dimethylpyrazol-1-yl)methane]cadmium(II)}]-di-μ-dicyanamidato], $[Cd_2(C_2N_3)_4(C_{11}H_{16}N_4)_2]_n$, each Cd atom is octahedrally coordinated by two N atoms from one dmpzm ligand and four N atoms from four bridging dicyanamide (dca) anions. Two Cd atoms are bridged by a pair of dca anions, forming a dimeric $[Cd_2(\mu\text{-dca})_2(dmpzm)_2]$ unit. Another two pairs of dca anions further link this unit with neighboring units to form a brick-wall layer parallel to (100). A C—H$\cdots$N interaction between the methylene group of one dmpzm ligand in one layer and a coordinating N atom of a dca ligand in an adjacent layer completes a three-dimensional network.

Comment

Cadmium(II) is known to react with N-donor ligands to form various cadmium(II) complexes which exhibit interesting structural diversity (Sessler *et al.*, 1988; Constable *et al.*, 1991; Plater *et al.*, 2000; Bartoszak-Adamska *et al.*, 2002; Pedrido *et al.*, 2003; Granifo *et al.*, 2004; Liu *et al.*, 2004; Su *et al.*, 2004). Most cadmium complexes of N-donor ligands are those derived from planar aromatic *N*,*N*′-bidentate ligands such as 4,4′-bipyridine (4,4′-bipy) and 1,10-phenanthroline (phen) (Long *et al.*, 1993; Neels & Stoeckli-Evans, 1999; Ye *et al.*, 2000; Yang *et al.*, 2003). However, the chemistry of cadmium complexes of the flexible *N*,*N*′-bidentate bis(pyrazolyl)alkane ligands has been less well explored (McMorran *et al.*, 2002; Pettinari & Pettinari, 2005; Cheng *et al.*, 2006).


(I)


(II)

We have recently been involved in studies on the synthesis and luminescent properties of metal complexes of bis(3,5-dimethylpyrazol-1-yl)methane (dmpzm) (Xu *et al.*, 2005; Cheng *et al.*, 2006; Li *et al.*, 2006). In the case of cadmium, we isolated the first cadmium–dmpzm complex, $[Cd_2Cl_4(dmpzm)_2]$, from the reaction of $CdCl_2$ with dmpzm, and reported the crystal structure (Cheng *et al.*, 2006). In light of the fact that isothiocyanate and dicyanamide (dca) are versatile linkers for the construction of coordination polymers (Luo, Hong, Cao *et al.*, 2002; Luo, Hong, Weng *et al.* 2002; Batten & Murray, 2003; Dong *et al.*, 2003; Luo *et al.*, 2004), we studied the analogous reactions of $CdCl_2$ with dmpzm in the presence of NH_4SCN or sodium dicyanamide (Na–dca) in order to produce Cd–dmpzm coordination polymers linked by isothiocyanate or dicyanamide anions. We isolated one mononuclear complex, $[Cd(NCS)_2(dmpzm)_2]$, (I), and one two-dimensional polymeric

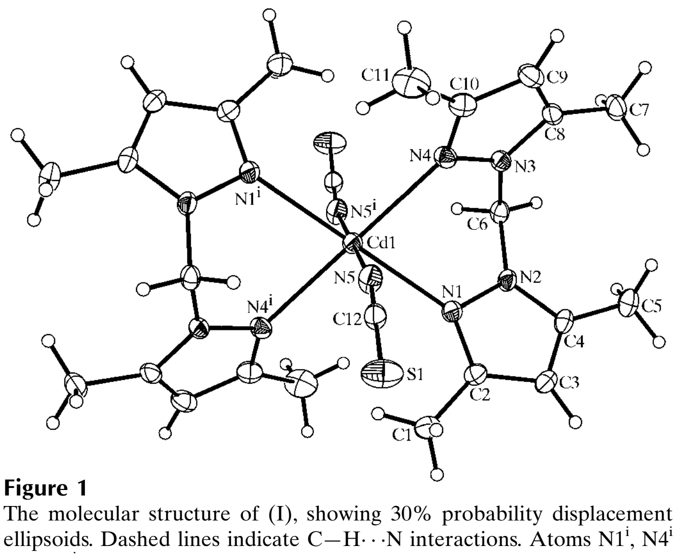


Figure 1
The molecular structure of (I), showing 30% probability displacement ellipsoids. Dashed lines indicate C—H$\cdots$N interactions. Atoms N1^i, N4^i and N5^i and unlabeled atoms are related to atoms N1, N4 and N5 and other labeled atoms by the symmetry operation ($-x$, $-y$, $1-z$).

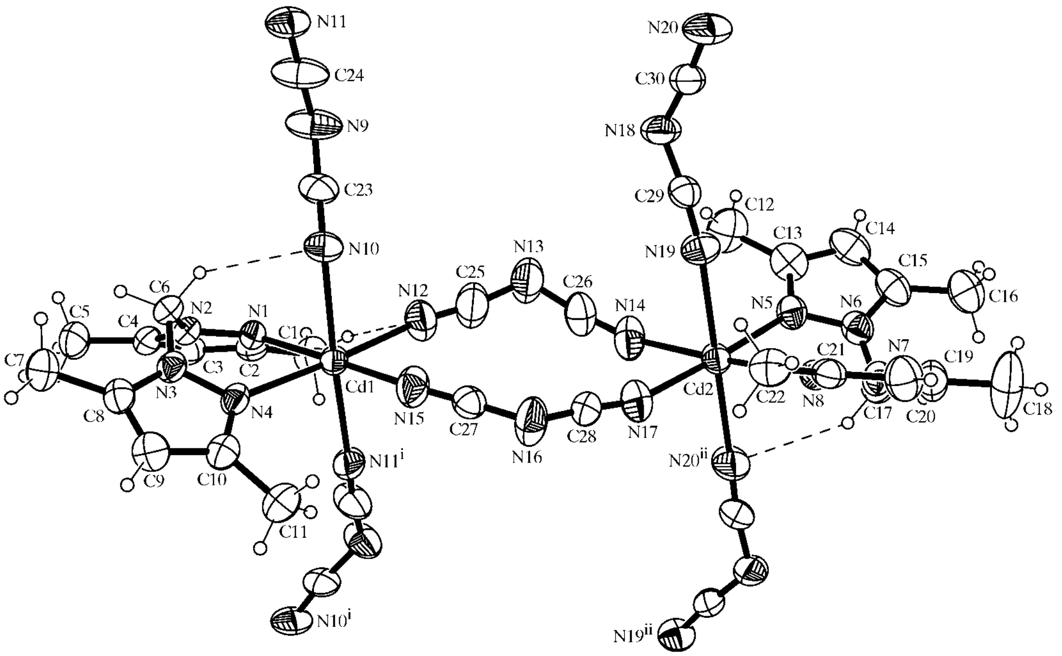


Figure 2
The repeating dimeric unit of (II), showing 30% probability displacement ellipsoids [symmetry codes: (i) $x, -y + \frac{3}{2}, z - \frac{1}{2}$; (ii) $x, -y + \frac{1}{2}, z - \frac{1}{2}$].

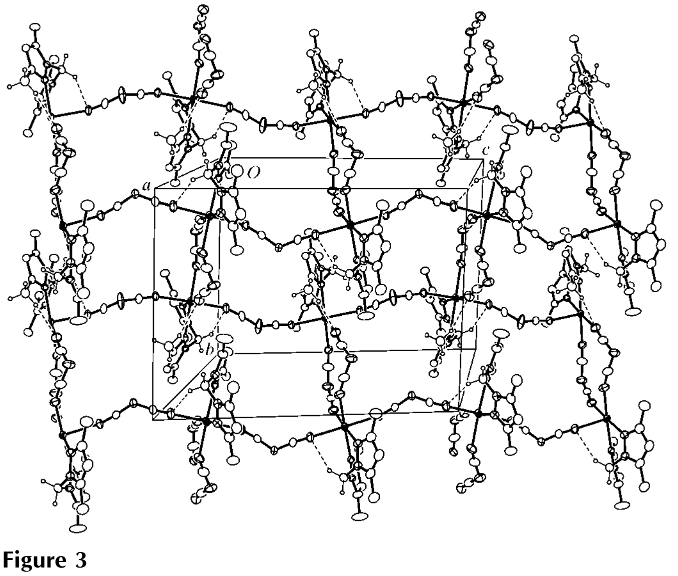


Figure 3
The brick-wall layer of (II), parallel to (100). The dashed lines indicate C—H···N interactions.

complex, $[Cd_2(\mu\text{-dca})_4(dmpzm)_2]_n$, (II). We report here the crystal structures of (I) and (II).

The asymmetric unit of (I) contains half of the $[Cd(NCS)_2(dmpzm)_2]$ molecule. As shown in Fig. 1, atom Cd1 lies on an inversion center and is coordinated by four N atoms [N1, N1^i, N4 and N4^i; symmetry code: (i) $-x, -y, -z + 1$; Table 1] from two dmpzm ligands, located in the equatorial plane, and two N atoms (N5 and N5^i) from the two isothiocyanate ligands in the apical sites, thereby forming a slightly distorted CoN_6 octahedral coordination geometry. The Cd—N(isothiocyanate) bond distance [2.305 (2) Å] is close to that observed in $[Cd(NCS)_2L_4]$ [2.312 (4) Å; L is 4,4,5,5-tetramethyl-2-(4-pyridyl)imidazoline-1-oxyl; Fettouhi *et al.*, 2002] and intermediate between that in $[Cd(NCS)_2L]$ [2.217 (4) Å; L is 3,3′-iminobis(*N*,*N*-dimethylpropylamine); Sain *et al.*, 2003] and that in $[Cd(NCS)_2L_2]$ [2.378 (2) Å; L is isopropyl-2-methylpropane-1,2-diamine; Pariya *et al.*, 1996]. Each dmpzm ligand adopts an extended and twisted *exo–anti* conformation, and coordinates to one Cd center in an *N*,*N*′-bidentate fashion, forming a six-membered $C(N—N)_2Cd$ chelate ring. The average Cd—N(dmpzm) bond distance [2.399 (3) Å] is comparable to that of the corresponding bonds in $[Cd(NCS)_2L_2]$ [2.389 (4) (L is 2,2′-bipyridine; Rodesiler *et al.*, 1984) and 2.382 (2) Å (L is isopropyl-2-methylpropane-1,2-diamine; Pariya *et al.*, 1996)]. Atom H6*B* from the CH_2 group of the dmpzm ligand interacts with atom N5^i of the isothiocyanate ligand to afford an intramolecular C—H···N contact (Table 2). There are no other evident interactions in the crystal structure of (I).

The asymmetric unit of (II) contains the dimeric $[Cd_2(\mu\text{-dca})_4(dmpzm)_2]$ unit (Fig. 2). The dimeric unit contains two $[Cd(dmpzm)]^{2+}$ fragments connected by a pair of dca bridges. The Cd1···Cd2 separation within the dimer unit is 7.595 (5) Å. Another two pairs of dca anions further link this unit with the neighboring units *via* Cd—μ-dca—Cd bridges to form a brick-wall-type layer parallel to (100) (Fig. 3). The Cd1···Cd1^i contact [symmetry code: (i) $x, -y + \frac{3}{2}, z - \frac{1}{2}$] between adjacent dimeric units is 8.900 (5) Å. Atoms Cd1 and Cd2 have a slightly distorted CoN_6 octahedral coordination geometry (Table 3z). The average Cd—N(dmpzm) bond distance [2.359 (4) Å] is comparable to that in (I). The mean Cd—N(dca) bond length [2.316 (4) Å] is close to those observed in $[Cd(dca)_2(2,2'\text{-bipy})]_n$ [2.313 (3) Å; Luo, Hong, Cao *et al.*, 2002] and $[Cd(dca)_2(phen)]_n$ [2.324 (4) Å; Luo, Hong, Cao *et al.*, 2002], but slightly longer than that in *cis*-$[Cd(dca)_2(phen)_2]$ [2.251 (2) Å; Lan *et al.*, 2005]. The N—Cd—N bite angle of 81.82 (13)° for Cd1 or 83.56 (13)° for Cd2

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is larger than that found in complex (I). The central C—N—C angles of the dca ligands [120.9 (6)–121.0 (5)°] are normal relative to those in $[Cd(dca)_2(2,2'\text{-bipy})]_n$ and $[Cd(dca)_2(phen)]_n$.

In (II), three unique C—H···N interactions (Table 4) exist between the N atoms of some dca anions and the methyl or methylene groups of immediately adjacent dmpzm ligands (Fig. 2). A further C—H···N interactions [C17—H17*A*···N14^{iii}; symmetry code: (iii) $-x+1, y-\frac{1}{2}, -z+\frac{1}{2}$] between the methylene group of one dmpzm ligand in one layer and a coordinating N atom of a dca ligand in an adjacent layer completes a three-dimensional network.

Experimental

To a solution of $CdCl_2\cdot 2.5H_2O$ (22.8 mg, 0.1 mmol) and NH_4SCN (11.4 mg, 0.2 mmol) in methanol (5 ml) was added a solution of dmpzm (0.0408 g, 0.2 mmol) in methanol (5 ml). The mixture was stirred at room temperature for 3 h and then filtered. Slow evaporation of the solvent from the filtrate gave rise to colorless crystals of (I) (yield 90%). Analysis found: C 45.38, H 5.01, N 21.83%; calculated for $C_{24}H_{32}CdN_{10}S_2$: C 45.24, H 5.06, N 21.98%. For the preparation of (II), a solution of dmpzm (0.0204 g, 0.1 mmol) in methanol (5 ml) was added to a solution of $CdCl_2\cdot 2.5H_2O$ (22.8 mg, 0.1 mmol) and sodium dicyanamide (17.8 mg, 0.2 mmol) in methanol (5 ml). The mixture was stirred at ambient temperature for 4 h and then filtered. Slow evaporation of the solvent from the filtrate afforded colorless crystals of (II) (yield 82%). Analysis found: C 40.29, H 3.52, N 31.35%; calculated for $C_{30}H_{32}Cd_2N_{20}$: C 40.15, H 3.59, N 31.21%.

Compound (I)

Crystal data

$[Cd(NCS)_2(C_{11}H_{16}N_4)_2]$
$M_r = 637.15$
Monoclinic, $P2_1/c$
$a = 10.117$ (2) Å
$b = 15.951$ (3) Å
$c = 9.858$ (2) Å
$\beta = 114.33$ (3)°
$V = 1449.6$ (6) Å^3

$Z = 2$
$D_x = 1.460$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.93$ mm^{-1}
$T = 193$ (2) K
Block, colorless
0.40 × 0.30 × 0.11 mm

Data collection

Rigaku Mercury diffractometer
ω scans
Absorption correction: multi-scan (Jacobson, 1998)
$T_{min} = 0.708$, $T_{max} = 0.905$

14037 measured reflections
2645 independent reflections
2513 reflections with $I > 2\sigma(I)$
$R_{int} = 0.027$
$\theta_{max} = 25.4°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.065$
$S = 1.20$
2645 reflections
173 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0196P)^2 + 1.3298P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.40$ e Å^{-3}
$\Delta\rho_{min} = -0.26$ e Å^{-3}

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

Cd1—N5	2.305 (2)	Cd1—N1	2.404 (2)
Cd1—N4	2.393 (2)		
N5—Cd1—N4	89.76 (8)	N4—Cd1—N1	79.09 (7)
N5—Cd1—N1	88.32 (8)		

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

D—H···A	D—H	H···A	D···A	D—H···A
C6—H6*B*···N5^{i}	0.99	2.43	3.288 (3)	145

Symmetry code: (i) $-x, -y, -z+1$.

Compound (II)

Crystal data

$[Cd_2(C_2N_3)_4(C_{11}H_{16}N_4)_2]$
$M_r = 897.56$
Monoclinic, $P2_1/c$
$a = 17.756$ (4) Å
$b = 12.883$ (3) Å
$c = 17.637$ (4) Å
$\beta = 110.44$ (3)°
$V = 3780.5$ (17) Å^3

$Z = 4$
$D_x = 1.577$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 1.18$ mm^{-1}
$T = 193$ (2) K
Block, colorless
0.30 × 0.28 × 0.10 mm

Data collection

Rigaku Mercury diffractometer
ω scans
Absorption correction: multi-scan (Jacobson, 1998)
$T_{min} = 0.719$, $T_{max} = 0.891$

41781 measured reflections
8663 independent reflections
7222 reflections with $I > 2\sigma(I)$
$R_{int} = 0.048$
$\theta_{max} = 27.5°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.058$
$wR(F^2) = 0.114$
$S = 1.12$
8663 reflections
465 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0314P)^2 + 8.9035P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.24$ e Å^{-3}
$\Delta\rho_{min} = -0.98$ e Å^{-3}

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

Cd1—N12	2.297 (5)	Cd2—N17	2.297 (5)
Cd1—N11^{i}	2.308 (4)	Cd2—N14	2.310 (5)
Cd1—N15	2.314 (4)	Cd2—N19	2.326 (4)
Cd1—N10	2.343 (4)	Cd2—N20^{ii}	2.327 (4)
Cd1—N4	2.344 (4)	Cd2—N8	2.329 (4)
Cd1—N1	2.381 (4)	Cd2—N5	2.382 (4)
N12—Cd1—N15	88.39 (18)	N17—Cd2—N19	90.58 (17)
N12—Cd1—N10	85.37 (18)	N14—Cd2—N19	87.48 (17)
N15—Cd1—N10	90.79 (16)	N17—Cd2—N8	97.59 (16)
N12—Cd1—N4	176.41 (16)	N14—Cd2—N8	175.36 (16)
N15—Cd1—N4	94.95 (15)	N19—Cd2—N8	91.72 (14)
N10—Cd1—N4	93.26 (15)	N17—Cd2—N5	177.66 (16)
N12—Cd1—N1	94.82 (16)	N14—Cd2—N5	91.83 (16)
N15—Cd1—N1	176.60 (15)	N19—Cd2—N5	87.35 (15)
N10—Cd1—N1	88.36 (15)	N8—Cd2—N5	83.56 (13)
N4—Cd1—N1	81.82 (13)	C26—N13—C25	120.9 (6)
N17—Cd2—N14	86.99 (18)	C27—N16—C28	121.0 (5)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1*A*···N12	0.98	2.56	3.460 (8)	153
C6—H6*B*···N10	0.99	2.49	3.329 (7)	143
C17—H17*A*···N14^{iii}	0.99	2.53	3.302 (7)	134
C17—H17*B*···N20^{ii}	0.99	2.50	3.341 (7)	143

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

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The methy H atoms were constrained to an ideal geometry, with C—H = 0.98 Å and U_{iso}(H) = 1.5U_{eq}(C), but were allowed to rotate freely about the parent C—C bonds. All other H atoms were positioned geometrically and treated as riding, with C—H = 0.95–0.98 Å and U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(methyl C).

For both compounds, data collection: *CrystalClear* (Rigaku/MSC, 2001); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Rigaku/MSC, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); 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: OB3022). Services for accessing these data are described at the back of the journal.

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