metal-organic compounds

Dichloro[(3,5-dimethyl-1*H*-pyrazol-1-yl)methane]zinc(II) and di-*μ*-chloro-bis{chloro[(3,5-dimethyl-1*H*-pyrazol-1-yl)methane]cadmium(II)}

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The Zn atom in dichloro[(3,5-dimethyl-1*H*-pyrazol-1-yl)methane]zinc(II), [ZnCl$_2$(C$_{11}$H$_{16}$N$_4$)], (I), is tetrahedrally coordinated by two N atoms from one bis(3,5-dimethylpyrazolyl)methane ligand and two terminal Cl atoms. The molecule has no crystallographic symmetry. One H atom of the CH$_2$ group of the bis(3,5-dimethylpyrazolyl)methane ligand interacts with a Cl atom of an adjacent molecule to yield intermolecular C—H···Cl contacts, thereby forming a one-dimensional zigzag chain extending along the *b* axis. On the other hand, in di-*μ*-chloro-bis{chloro[(3,5-dimethyl-1*H*-pyrazol-1-yl)methane]cadmium(II)}, [Cd$_2$Cl$_4$(C$_{11}$H$_{16}$N$_4$)$_2$], (II), each of the two crystallographically equivalent Cd atoms is pentacoordinated by two N atoms from one bis(3,5-dimethylpyrazolyl)methane ligand, and by one terminal and two bridging Cl$^-$ anions. The molecule has a crystallographic centre of symmetry located at the mid-point of the Cd···Cd line. One H atom of the CH$_2$ group of the bis(3,5-dimethylpyrazolyl)methane ligand interacts with a Cl atom of an adjacent molecule to produce pairwise intermolecular C—H···Cl contacts, thereby affording chains of molecules running along the *c* axis.

Comment

It is well known that group 12 metals react with *N*-donor ligands to form various adducts, and these compounds exhibit diversity in their structural chemistry (Neels & Stoeckli-Evans, 1999; Erxleben, 2001; Kaminskaia *et al.*, 2000; Kleywegt *et al.*, 1985; Pedrido *et al.*, 2003; Patra & Goldberg, 2002). Among numerous *N*-donor ligands, bis(pyrazol-1-yl)alkanes, serving as flexible bidentate ligands, have been reported to form stable chelates with group 12 elements (Pettinari & Pettinari, 2005; Mann *et al.*, 1998; Bovio *et al.*, 1992). In the case of bis(3,5-dimethylpyrazol-1-yl)methane (dmpzm), however, the chem-

istry of its zinc and cadmium complexes is relatively unexplored. For example, several zinc complexes of dmpzm {*e.g.* [Zn*X*$_2$(dmpzm)], where *X* = Cl$^-$, Br$^-$, I$^-$, CF$_3$CO$_2$$^-$ or OAc$^-$, or [Zn(dmpzm)$_2$*X*$_2$], where *X* = ClO$_4$$^-$, NO$_3$$^-$, or BF$_4$$^-$} have been prepared (Reedijk & Verbiest, 1979; Leonesi *et al.*, 1987), but their crystal structures have not been reported to date. To our knowledge, there is no synthetic or structural information on any cadmium complex of the dmpzm ligand. We have recently become interested in the preparation of transition metal complexes of dmpzm (Xu *et al.*, 2005). Curious about the chemistry of zinc/cadmium complexes of dmpzm, we carried out the reaction of ZnCl$_2$ or CdCl$_2$ with dmpzm and the two title complexes, [ZnCl$_2$(dmpzm)], (I), and [Cd$_2$(μ-Cl)Cl(dmpzm)]$_2$, (II), were isolated therefrom. We report here the crystal structures of complexes (I) and (II).
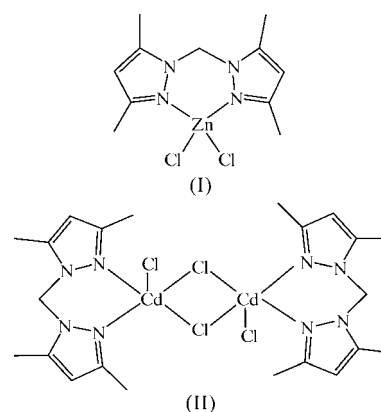
The asymmetric unit of (I) contains a discrete [ZnCl$_2$-(dmpzm)] molecule. Compound (I) may be viewed as having a 'butterfly'-shaped structure (Fig. 1), which resembles that of [ZnBr$_2$*L*] [*L* is bis(3,4,5-trimethylpyrazol-1-yl)methane; Pettinari *et al.*, 1998]. There is no crystallographic symmetry in this molecule. Atom Zn1 is bound to two N atoms from the dmpzm ligand and two terminal Cl atoms, forming a distorted tetrahedral geometry, with the angles around Zn1 being in the range 89.33 (5)–115.20 (4)°. The mean Zn—N bond distance [2.0588 (12) Å] is comparable with that in [ZnCl$_2$*L*$_2$] [2.052 (4) Å; *L* is 4-acetylpyridine; Steffen & Palenik, 1977],
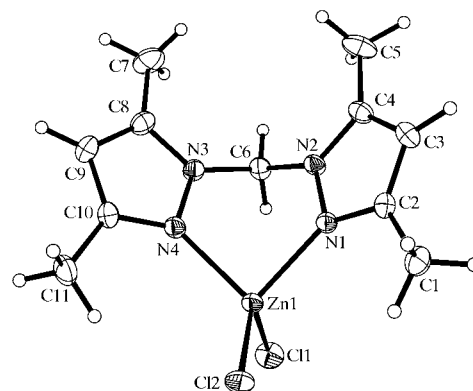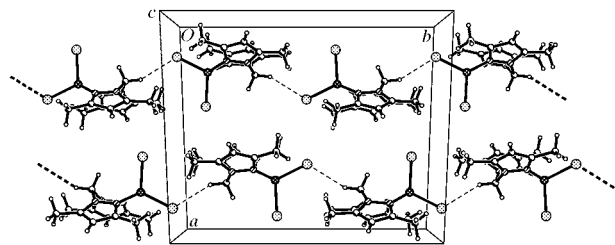

Figure 1
A view of the molecule of complex (I), with displacement ellipsoids drawn at the 30% probability level. H atoms are shown as small spheres of arbitrary radii.

but shorter than those in [ZnBr$_2$L] [2.076 (7) Å; L is bis(3,4,5-trimethylpyrazol-1-yl)methane; Pettinari *et al.*, 1998] or [ZnCl$_2$L] [2.132 (2) Å; L is 2,2-bis(pyrazol-1-yl)propane; Bovio *et al.*, 1992]. The mean Zn—Cl bond length [2.2184 (4) Å] is close to the values observed in [ZnCl$_2$L] [2.211 (3) Å; L is 4-acetylpyridine; Steffen & Palenik, 1977], [ZnCl$_2$L] [2.219 (2) Å; L is 2,2-bis(pyrazol-1-yl)propane; Bovio *et al.*, 1992] and [ZnCl$_3$L] [2.240 (5) Å; L is 8-aza-adeninium; Purnell & Hodgson, 1977]. The N1—Zn1—N4 bite angle of 89.33 (5)° in (I) is comparable with that observed in [ZnCl$_2$L] [89.47°; L is 2,2-bis(pyrazol-1-yl)propane; Bovio *et al.*, 1992].

Atom H6B from the CH$_2$ group of each dmpzm ligand in (I) interacts with atom Cl2 of an adjacent molecule to afford intermolecular C—H···Cl contacts (Fig. 2), thereby forming a
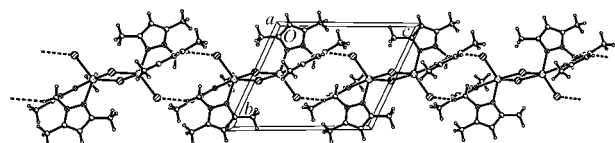

Figure 2
A packing diagram for (I), viewed approximately down the *b* axis, showing the one-dimensional zigzag chain formed by C—H···Cl interactions.
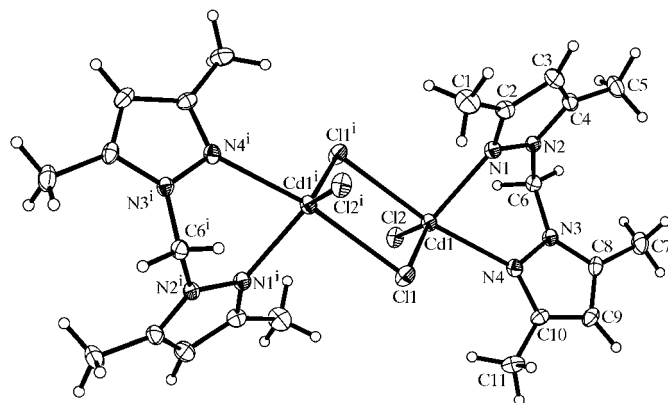
Figure 3
A view of the molecule of complex (II), with displacement ellipsoids drawn at the 30% probability level. H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (i) −x, 1 − y, −z.]

Figure 4
A packing diagram for (II), viewed approximately down the *c* axis, showing the one-dimensional chain formed by C—H···Cl interactions.

one-dimensional zigzag chain extending along the *b* axis (Table 2). The H···Cl contact distance is 2.77 (2) Å, which is comparable with those observed in [ZnCl$_2$L] {2.74 (2) and 2.83 (2) Å; L is 4-methyl-2,6-bis[(S)-(+)-1-phenylethylimino-methyl]phenol; Prabhakar *et al.*, 2005}, and in *trans,cis,cis*-[RuCl$_2$(Meim)$_2$(SbPh$_3$)$_2$] [2.69 (1) and 2.94 (1) Å; Meim is *N*-methylimidazole] and *trans,cis,cis*-[RuCl$_2$(Mepym)$_2$(SbPh$_3$)$_2$] [2.95 (1) and 2.96 (1) Å; Mepym is 4-methylpyrimidine; Cini *et al.*, 2002].

The asymmetric unit of (II) contains one-half of the dimeric molecule [Cd(μ-Cl)Cl(dmpzm)]$_2$. As shown in Fig. 3, the structure contains a dimetallocyclic Cd$_2$Cl$_2$ core with a crystallographic centre of inversion at the mid-point of the Cd1···Cd1^i line [symmetry code: (i) −x, 1 − y, −z]. Each Cd atom has a slightly distorted trigonal–bipyramidal geometry, coordinated by two N atoms from the dmpzm ligand, a terminal Cl atom and two bridging Cl atoms. Atoms Cl1^i and N4 are in axial positions, while atoms Cl1, Cl2 and N1 are in equatorial positions. The Cl1^i—Cd1—N4 bond angle is 171.52 (4)°. The two terminal Cl atoms have *trans* orientations with respect to the planar Cd$_2$Cl$_2$ core. The dinuclear Cd$_2$Cl$_2$ core is asymmetric, as the Cd1—Cl1 and Cd1—Cl1^i bond distances are 2.4649 (7) and 2.7322 (9) Å, respectively, while the Cd1—Cl1—Cd1^i and Cl1—Cd1—Cl1^i angles are 94.68 (2) and 85.32 (2)°, respectively. The two asymmetric Cd—Cl distances are common for compounds containing a Cd$_2$Cl$_2$ core, as found in [CdCl$_2$L]$_2$ [2.487 (2) and 2.821 (2) Å; L is 1-(5,6-dimethylbenzimidiazol-2-yl)-3-(benzimidazol-2-yl)-2-thiapropane; Matthews *et al.*, 1998] and [CdCl$_2$L]$_2$ [2.537 (1) and 2.672 (1) Å; L is 3-amino-6,6′-dimethyl-2,2′-bipyridine; Long *et al.*, 1993]. The Cd1···Cd1^i contact of 3.826 (2) Å in (II) is too long to include any metal–metal interaction. Each dmpzm ligand adopts an extended and twisted *exo–anti* conformation and coordinates to one Cd centre in an *N,N′*-bidentate fashion, forming a six-membered C(N–N)$_2$Cd chelate ring. The average Cd—N bond distance [2.3467 (18) Å] is close to the values observed in [CdCl$_2$L]$_2$ [2.397 (2) Å; L is 1,4,7-triazacyclononane; Zompa *et al.*, 1995] and [CdCl$_2$L]$_2$ [2.367 (3) Å; L is *cis*-3,5-diaminopiperidine; Pauly *et al.*, 2000]. The N1—Cd1—N4 bite angle of 79.00 (6)° is normal compared with [CdCl$_2$L$_2$(H$_2$O)$_2$]$_2$ (80.71°; L is di-2-pyridylamine; Pickardt & Staub, 1999].

Each Cl2 atom of (II) interacts with the methylene group of the dmpzm ligand in an adjacent molecule in an afford pairwise intermolecular C—H···Cl contacts (Table 4), thereby affording chains of molecules running along the *c* axis (Fig. 4).

Experimental

To a solution of ZnCl$_2$ (0.136 g, 1 mmol) in a mixture of methanol and water (9:1 *v/v*, 10 ml) was added a solution of dmpzm (0.20 g, 1 mmol) in methanol (10 ml). A large amount of a white precipitate formed immediately. After stirring for 30 min, the precipitate was filtered off, washed with diethyl ether (3 × 5 ml) and dried *in vacuo*. Colourless prisms of [ZnCl$_2$(dmpzm)], (I), were obtained by recrystallization of the precipitate from a solution in dimethylformamide (yield 0.31 g, 91% based on Zn). Analysis found: C 38.72, H 4.73, N 15.96%;

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calculated for $C_{11}H_{16}Cl_2N_4Zn$: C 38.69, H 4.70, N 16.25%. IR (KBr, ν, cm^{-1}): 3134 (w), 3017 (m), 2930 (w), 1558 (s), 1467 (m), 1392 (s), 1380 (s), 1280 (s), 1051 (m), 1004 (w), 829 (m),809 (m), 677 (m).

To a solution of $CdCl_2 \cdot 2.5H_2O$ (0.228 g, 1 mmol) in a mixture of methanol and water (9:1 v/v, 10 ml) was added a solution of dmpzm (0.20 g, 1 mmol) in methanol (10 ml). The mixture was stirred at room temperature for 30 min. Slow evaporation of the solvents from the resulting solution produced colourless prisms of $[CdCl_2(dmpzm)]_2$, (II), which were collected by filtration, washed thoroughly with Et_2O and dried in air (yield 0.67 g, 87% based on Cd). Analysis found: C 34.11, H 4.21, N 13.18%; calculated for $C_{22}H_{32}Cd_2Cl_4N_8$: C 34.08, H 4.16, N 14.46%. IR (KBr, ν, cm^{-1}): 3124 (w), 3022 (w), 2925 (w), 1558 (s), 1464 (s), 1390 (s), 1281 (s), 1041 (m), 989 (w), 822 (m), 794 (m), 676 (m).

Compound (I)

Crystal data

$[ZnCl_2(C_{11}H_{16}N_4)]$	Mo $K\alpha$ radiation
$M_r = 340.55$	Cell parameters from 6686
Monoclinic, $C2/c$	reflections
$a = 14.9018\,(17)$ Å	$\theta = 3.0–27.5°$
$b = 16.7328\,(17)$ Å	$\mu = 2.07$ mm^{-1}
$c = 12.5546\,(14)$ Å	$T = 193\,(2)$ K
$\beta = 113.446\,(2)°$	Block, colourless
$V = 2872.0\,(5)$ Å^3	$0.50 \times 0.40 \times 0.38$ mm
$Z = 8$	
$D_x = 1.575$ Mg m^{-3}	

Data collection

Rigaku Mercury diffractometer	3119 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.018$
Absorption correction: multi-scan	$\theta_{max} = 27.5°$
(Jacobson, 1998)	$h = -19 \rightarrow 19$
$T_{min} = 0.382$, $T_{max} = 0.456$	$k = -21 \rightarrow 21$
15701 measured reflections	$l = -13 \rightarrow 16$
3291 independent reflections	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.024$	$\Delta\rho_{max} = 0.31$ e Å^{-3}
$wR(F^2) = 0.064$	$\Delta\rho_{min} = -0.63$ e Å^{-3}
$S = 1.04$	Extinction correction: *SHELXL97*
3291 reflections	(Sheldrick, 1997)
169 parameters	Extinction coefficient: 0.0038 (2)
H-atom parameters constrained	
$w = 1/[\sigma^2(F_o^2) + (0.038P)^2$	
$+ 2.2138P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

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

Zn1—N1	2.0569 (12)	Zn1—Cl2	2.2164 (4)
Zn1—N4	2.0616 (12)	Zn1—Cl1	2.2204 (5)
N1—Zn1—N4	89.33 (5)	N1—Zn1—Cl1	110.08 (4)
N1—Zn1—Cl2	114.99 (4)	N4—Zn1—Cl1	111.12 (4)
N4—Zn1—Cl2	115.20 (4)	Cl2—Zn1—Cl1	113.738 (17)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C6—H6$B\cdots$Cl2^i	0.99	2.77	3.6875 (15)	154

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

Compound (II)

Crystal data

$[Cd_2Cl_4(C_{11}H_{16}N_4)_2]$	$D_x = 1.794$ Mg m^{-3}
$M_r = 775.16$	Mo $K\alpha$ radiation
Triclinic, $P\bar{1}$	Cell parameters from 3251
$a = 7.7033\,(17)$ Å	reflections
$b = 9.232\,(2)$ Å	$\theta = 3.3–25.3°$
$c = 11.513\,(2)$ Å	$\mu = 1.88$ mm^{-1}
$\alpha = 112.752\,(19)°$	$T = 193\,(2)$ K
$\beta = 102.34\,(2)°$	Block, colourless
$\gamma = 97.28\,(3)°$	$0.54 \times 0.21 \times 0.20$ mm
$V = 717.4\,(3)$ Å^3	
$Z = 1$	

Data collection

Rigaku Mercury diffractometer	2487 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.016$
Absorption correction: multi-scan	$\theta_{max} = 25.4°$
(Jacobson, 1998)	$h = -9 \rightarrow 9$
$T_{min} = 0.417$, $T_{max} = 0.684$	$k = -11 \rightarrow 11$
7007 measured reflections	$l = -13 \rightarrow 13$
2597 independent reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0223P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.018$	$+ 0.3284P]$
$wR(F^2) = 0.044$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.10$	$(\Delta/\sigma)_{max} = 0.001$
2597 reflections	$\Delta\rho_{max} = 0.53$ e Å^{-3}
168 parameters	$\Delta\rho_{min} = -0.44$ e Å^{-3}
H-atom parameters constrained	

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

Cd1—N1	2.2847 (19)	Cd1—Cl1	2.4649 (7)
Cd1—N4	2.4088 (18)	Cd1—Cl1^i	2.7322 (9)
Cd1—Cl2	2.4616 (9)	Cl1—Cd1^i	2.7322 (9)
N1—Cd1—N4	79.00 (6)	N1—Cd1—Cl1^i	92.87 (5)
N1—Cd1—Cl2	116.72 (5)	N4—Cd1—Cl1^i	171.52 (4)
N4—Cd1—Cl2	89.61 (5)	Cl2—Cd1—Cl1^i	91.95 (3)
N1—Cd1—Cl1	114.00 (5)	Cl1—Cd1—Cl1^i	85.32 (2)
N4—Cd1—Cl1	100.11 (4)	Cd1—Cl1—Cd1^i	94.68 (2)
Cl2—Cd1—Cl1	129.28 (3)		

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

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C6—H6$A\cdots$Cl2^{ii}	0.99	2.77	3.666 (2)	151

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

All H atoms were placed in geometrically idealized positions, with C—H = 0.98 Å for methyl groups, 0.99 Å for methylene groups or 0.95 Å for ring CH groups, and constrained to ride on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}(C)$, or $1.5U_{eq}(C)$ for the methyl groups.

For both compounds, data collection: *CrystalClear* (Rigaku, 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) and *SHELXL97*; software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1428). Services for accessing these data are described at the back of the journal.

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