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Di-μ-chloro-bis{chloro[3,5-dimethyl-1-(thiocarbamoyl)pyrazole-κ^2N^2,S]cadmium(II)}

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Transition metal complexes with pyrazole-based ligands, Part XX

Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.004 Å
R factor = 0.023
wR factor = 0.053
Data-to-parameter ratio = 22.6

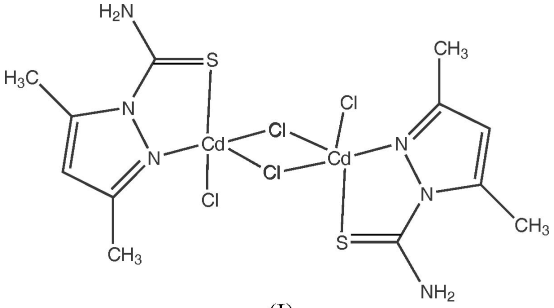
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The crystal structure of the title compound, $[Cd_2Cl_4(C_6H_9N_3S)_2]$, has been determined. The compound is isomorphous with the previously reported Cu^{II} and Co^{II} complexes. It is centrosymmetric and contains binuclear molecular units with five-coordinate Cd atoms, doubly bridged by Cl atoms. The structure is stabilized by a two-dimensional network of hydrogen bonds involving the terminal Cl atoms as acceptors and thiocarbamoyl group N atoms as donors.

Comment

The complex of 3,5-dimethyl-1-(thiocarbamoyl)pyrazole with cadmium chloride was obtained as a part of our systematic studies on pyrazole-based complexes (Jaćimović *et al.*, 1999; Tomić *et al.*, 2000; Mészáros Szécsényi *et al.*, 2001; Mészáros Szécsényi, Leovac, Češljević *et al.*, 2003; Jaćimović *et al.*, 2003). The ligand 3,5-dimethyl-1-(thiocarbamoyl)pyrazole, *L*, was synthesized by a reaction of thiosemicarbazide with acetylacetone in an acidic aqueous solution and its crystal structure was recently reported (Kovács *et al.*, 2005).

The complexing ability of *L* was tested against a number of transition metal ions. The ligand has three potential donor atoms: the nitrogen of the pyrazole ring, the amino N atom and the S atom of the thiocarbamoyl group. In principle, it can take part in coordination as a bi- or monodentate neutral species (Radosavljevic Evans, Howard, Mészáros Szécsényi *et al.*, 2004; Radosavljević Evans, Howard, Howard *et al.*, 2004; Kovács *et al.*, 2005). In addition, there is a possibility of the amino-group deprotonation, resulting in complexes of non-electrolytic character (Mészáros Szécsényi *et al.*, 2003; Radosavljević Evans, Howard, Mészáros Szécsényi *et al.*, 2004). The molecular structure of the coordination complex formed depends primarily on the characteristic bonding preferences of the central metal ion and the nature of the anion.



(I)

The crystal structure of the title compound, $Cd_2L_2Cl_4$, (I), consists of discrete neutral binuclear units (Fig. 1). The Cd centres are doubly bridged by Cl atoms, with a Cd···Cd

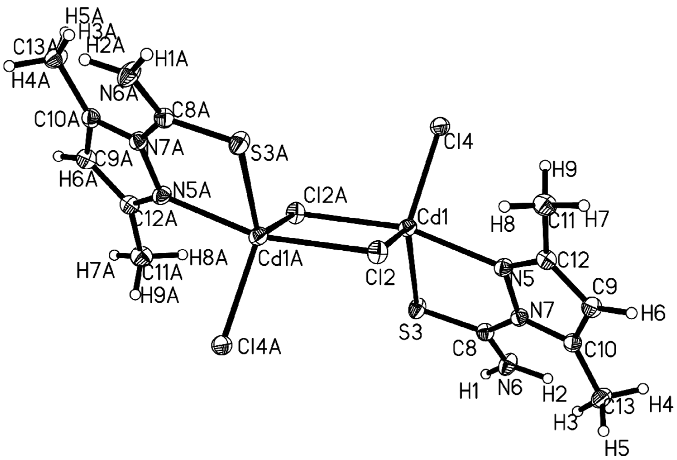


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The suffix A corresponds to the symmetry code ($-x$, $-y$, $1 - z$).

distance of 3.763 (1) Å. The molecule is centrosymmetric, but the bridges within the Cd_2Cl_2 core are asymmetric, with Cd—Cl distances of 2.5393 (7) and 2.6174 (7) Å, and a bridging angle of 93.70 (2)°.

The Cd atoms are five-coordinate. Ligand L acts as a neutral bidentate ligand, coordinating through the N atom of the pyrazole ring and the thiocarbamoyl S atom. The Cd coordination is completed by two bridging and one terminal Cl atom. Pentacoordinate geometry can be described using the distortion parameter τ (Addison *et al.*, 1984), where $\tau = 1$ corresponds to an ideal trigonal bipyramid and $\tau = 0$ to an ideal square pyramid. In the case of the title complex, $\tau = 0.69$, suggesting that the coordination of the Cd atom is best described as distorted trigonal bipyramidal. The degree of distortion is slightly higher than in the isomorphous Cu^{II} and Co^{II} complexes (τ values of 0.75 and 0.77, respectively; Radosavljević Evans, Howard, Howard *et al.*, 2004). The axial positions are occupied by a bridging Cl atom and the pyrazole nitrogen, with a Cl—Cd—N angle of 165.20 (6)°. The ligand bite angle is 75.10 (5)°, reflecting a larger degree of departure from the right angle expected for an ideal trigonal–bipyramidal environment than in the analogous Cu and Co complexes. Both the pyrazole ring and the thiocarbamoyl group are essentially planar, and they form a dihedral angle of 19.8 (5)°. The molecules are packed with the ligand pyrazole rings parallel (Fig. 2). Each terminal Cl atom acts as a hydrogen-bond acceptor for thiocarbamoyl NH groups in two adjacent molecules, with H···Cl distances of 2.34 and 2.47 Å (Table 2), giving rise to a two-dimensional hydrogen-bonding network in the structure.

Experimental

$CdCl_2 \cdot H_2O$ (0.20 g, 1 mmol) was suspended in MeOH (10 ml). 3,5-Dimethyl-1-(thiocarbamoyl)pyrazole (0.31 g, 2 mmol) was added to the suspension. The reaction mixture was heated under reflux. After 30 min of heating, the resulting clear solution was left at room temperature. About 3 h later, the white precipitate was filtered off, washed with MeOH and air-dried (yield: 0.14 g, 41%). Needle-shaped single crystals were obtained by recrystallization from MeOH.

Crystal data

$[Cd_2Cl_4(C_6H_9N_3S)_2]$
$M_r = 677.06$
Triclinic, $P\overline{1}$
$a = 7.7442$ (11) Å
$b = 8.6866$ (12) Å
$c = 8.7559$ (12) Å
$\alpha = 90.213$ (3)°
$\beta = 110.427$ (3)°
$\gamma = 103.074$ (3)°
$V = 535.46$ (13) Å^3

$Z = 1$
$D_x = 2.100$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3323 reflections
$\theta = 4.8$–60.1°
$\mu = 2.69$ mm^{-1}
$T = 150$ K
Needle, white
0.10 × 0.04 × 0.04 mm

Data collection

Bruker SMART APEX diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.841$, $T_{max} = 0.900$
6938 measured reflections

3102 independent reflections
2669 reflections with $I > 2\sigma(I)$
$R_{int} = 0.018$
$\theta_{max} = 30.1°$
$h = -10 \rightarrow 10$
$k = -12 \rightarrow 12$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.023$
$wR(F^2) = 0.053$
$S = 0.91$
2669 reflections
118 parameters
H-atom parameters not refined

$w = [1 - (F_o - F_c)^2/36\sigma^2(F)]^2/[2.82T_0(x) + 3.29T_1(x) + 1.36T_2(x)]$ where T$_i$ are Chebychev polynomials and $x = F_c/F_{max}$ (Watkin, 1994; Prince, 1982)
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.63$ e Å^{-3}
$\Delta\rho_{min} = -0.65$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cd1—Cl2^i	2.6174 (7)	N6—C8	1.312 (3)
Cd1—Cl2	2.5393 (7)	N7—C8	1.393 (3)
Cd1—S3	2.5768 (7)	N7—C10	1.396 (3)
Cd1—Cl4	2.4598 (7)	C9—C10	1.363 (4)
Cd1—N5	2.343 (2)	C9—C12	1.416 (4)
S3—C8	1.701 (3)	C10—C13	1.492 (4)
N5—N7	1.383 (3)	C11—C12	1.494 (4)
N5—C12	1.313 (3)		
Cl2^i—Cd1—Cl2	86.30 (2)	N7—N5—C12	106.5 (2)
Cl2^i—Cd1—S3	94.26 (3)	N5—N7—C8	118.6 (2)
Cl2—Cd1—S3	120.31 (3)	N5—N7—C10	109.9 (2)
Cl2^i—Cd1—Cl4	98.40 (2)	C8—N7—C10	131.4 (2)
Cl2—Cd1—Cl4	115.31 (2)	N7—C8—S3	122.18 (19)
S3—Cd1—Cl4	123.50 (2)	N7—C8—N6	117.9 (2)
Cl2^i—Cd1—N5	165.20 (6)	S3—C8—N6	119.9 (2)
Cl2—Cd1—N5	90.24 (6)	C10—C9—C12	106.8 (2)
S3—Cd1—N5	75.10 (5)	N7—C10—C9	106.2 (2)
Cl4—Cd1—N5	96.09 (6)	N7—C10—C13	125.8 (2)
Cd1^i—Cl2—Cd1	93.70 (2)	C9—C10—C13	128.0 (2)
Cd1—S3—C8	101.41 (9)	C11—C12—C9	128.2 (2)
Cd1—N5—N7	120.12 (16)	C11—C12—N5	121.2 (2)
Cd1—N5—C12	131.48 (17)	C9—C12—N5	110.7 (2)

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

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N6—H1···Cl4^{ii}	1.00	2.34	3.252 (3)	151
N6—H2···Cl4^{iii}	1.00	2.47	3.232 (3)	133

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

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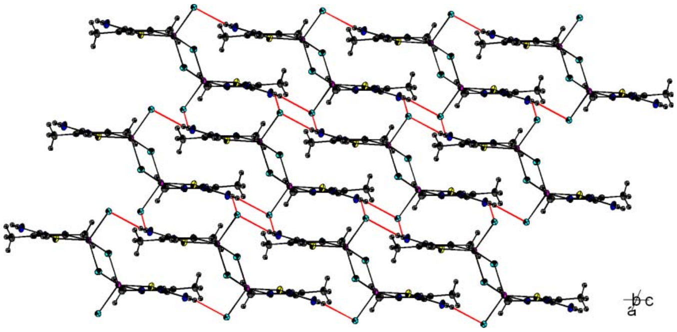

Figure 2
The packing scheme for (I); red lines represent N—H···Cl hydrogen bonds.

H atoms were placed geometrically after each cycle and treated as riding on their carrier atoms, with N/C—H = 1.00 Å and U_{iso}(H) = $1.2U_{eq}$(N,C).

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *ATOMS* (Dowty, 2000); software used to prepare material for publication: *CRYSTALS*.

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supporting information

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Di-μ-chloro-bis{chloro[3,5-dimethyl-1-(thiocarbamoyl)pyrazole-κ^2N^2,S]cadmium(II)}

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(I)

Crystal data

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$M_r = 677.06$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
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$b = 8.6866\ (12)$ Å
$c = 8.7559\ (12)$ Å
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$\beta = 110.427\ (3)°$
$\gamma = 103.074\ (3)°$
$V = 535.46\ (13)$ Å^3

$Z = 1$
$F(000) = 328$
$D_x = 2.100$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3323 reflections
$\theta = 4.8–60.1°$
$\mu = 2.69$ mm^{-1}
$T = 150$ K
Needle, white
0.10 × 0.04 × 0.04 mm

Data collection

Bruker SMART APEX diffractometer
Graphite monochromator
ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
$T_{min} = 0.841$, $T_{max} = 0.900$
6938 measured reflections

3102 independent reflections
2669 reflections with $I > 2\sigma(I)$
$R_{int} = 0.018$
$\theta_{max} = 30.1°$, $\theta_{min} = 2.4°$
$h = -10 \rightarrow 10$
$k = -12 \rightarrow 12$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.023$
$wR(F^2) = 0.053$
$S = 0.91$
2669 reflections
118 parameters
0 restraints
Primary atom site location: structure-invariant direct methods

Hydrogen site location: inferred from neighbouring sites
H-atom parameters not refined
$w = [1-(F_o-F_c)^2/36\sigma^2(F)]^2/[2.82T_0(x) + 3.29T_1(x) + 1.36T_2(x)]$ where T_i are Chebychev polynomials and $x = F_c/F_{max}$ (Watkin, 1994; Prince, 1982)
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.63$ e Å^{-3}
$\Delta\rho_{min} = -0.65$ e Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Cd1	0.21166 (3)	0.09432 (2)	0.68651 (2)	0.0173

Cl2	−0.09082 (9)	0.16729 (8)	0.50856 (8)	0.0205
S3	0.22169 (10)	−0.05068 (8)	0.94454 (8)	0.0211
Cl4	0.49608 (9)	0.21159 (8)	0.62265 (8)	0.0193
N5	0.2613 (3)	0.2944 (3)	0.8882 (3)	0.0175
N6	0.3136 (4)	0.0813 (3)	1.2401 (3)	0.0231
N7	0.2531 (3)	0.2553 (3)	1.0389 (3)	0.0162
C8	0.2656 (4)	0.1035 (3)	1.0841 (3)	0.0173
C9	0.2397 (4)	0.5060 (3)	1.0224 (3)	0.0196
C10	0.2381 (4)	0.3860 (3)	1.1223 (3)	0.0175
C11	0.2633 (4)	0.5273 (3)	0.7319 (3)	0.0233
C12	0.2552 (4)	0.4441 (3)	0.8791 (3)	0.0182
C13	0.2157 (4)	0.3880 (3)	1.2846 (3)	0.0231
H1	0.3246	−0.0261	1.2768	0.0209*
H2	0.3394	0.1718	1.3222	0.0209*
H3	0.1749	0.4869	1.2983	0.0301*
H4	0.3392	0.3889	1.3737	0.0294*
H5	0.1171	0.2926	1.2878	0.0294*
H6	0.2315	0.6163	1.0459	0.0241*
H7	0.2568	0.6397	0.7475	0.0285*
H8	0.1537	0.4721	0.6330	0.0285*
H9	0.3850	0.5258	0.7167	0.0285*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cd1	0.01818 (9)	0.01946 (9)	0.01484 (8)	0.00495 (6)	0.00638 (6)	0.00165 (6)
Cl2	0.0203 (3)	0.0195 (3)	0.0210 (3)	0.0074 (2)	0.0049 (2)	0.0008 (2)
S3	0.0304 (3)	0.0161 (3)	0.0166 (3)	0.0064 (2)	0.0077 (2)	0.0020 (2)
Cl4	0.0184 (3)	0.0215 (3)	0.0183 (3)	0.0044 (2)	0.0072 (2)	0.0016 (2)
N5	0.0220 (10)	0.0173 (10)	0.0140 (9)	0.0049 (8)	0.0075 (8)	0.0033 (7)
N6	0.0357 (13)	0.0198 (10)	0.0149 (10)	0.0106 (10)	0.0081 (9)	0.0035 (8)
N7	0.0175 (9)	0.0169 (10)	0.0139 (9)	0.0041 (8)	0.0053 (7)	0.0021 (7)
C8	0.0179 (11)	0.0166 (11)	0.0170 (11)	0.0042 (9)	0.0060 (9)	0.0025 (9)
C9	0.0203 (12)	0.0178 (11)	0.0222 (12)	0.0066 (9)	0.0082 (10)	0.0026 (9)
C10	0.0158 (10)	0.0178 (11)	0.0183 (11)	0.0038 (9)	0.0058 (9)	0.0001 (9)
C11	0.0273 (13)	0.0211 (12)	0.0226 (12)	0.0068 (10)	0.0098 (10)	0.0078 (10)
C12	0.0173 (11)	0.0186 (11)	0.0182 (11)	0.0046 (9)	0.0056 (9)	0.0037 (9)
C13	0.0305 (14)	0.0221 (12)	0.0210 (12)	0.0080 (11)	0.0135 (11)	0.0019 (10)

Geometric parameters (Å, º)

Cd1—Cl2^{i}	2.6174 (7)	N7—C10	1.396 (3)
Cd1—Cl2	2.5393 (7)	C9—C10	1.363 (4)
Cd1—S3	2.5768 (7)	C9—C12	1.416 (4)
Cd1—Cl4	2.4598 (7)	C9—H6	1.000
Cd1—N5	2.343 (2)	C10—C13	1.492 (4)
S3—C8	1.701 (3)	C11—C12	1.494 (4)
N5—N7	1.383 (3)	C11—H7	1.000

N5—C12	1.313 (3)	C11—H8	1.000
N6—C8	1.312 (3)	C11—H9	1.000
N6—H1	1.000	C13—H3	1.000
N6—H2	1.000	C13—H4	1.000
N7—C8	1.393 (3)	C13—H5	1.000

Cl2^{i}—Cd1—Cl2	86.30 (2)	S3—C8—N6	119.9 (2)
Cl2^{i}—Cd1—S3	94.26 (3)	C10—C9—C12	106.8 (2)
Cl2—Cd1—S3	120.31 (3)	C10—C9—H6	126.568
Cl2^{i}—Cd1—Cl4	98.40 (2)	C12—C9—H6	126.659
Cl2—Cd1—Cl4	115.31 (2)	N7—C10—C9	106.2 (2)
S3—Cd1—Cl4	123.50 (2)	N7—C10—C13	125.8 (2)
Cl2^{i}—Cd1—N5	165.20 (6)	C9—C10—C13	128.0 (2)
Cl2—Cd1—N5	90.24 (6)	C12—C11—H7	109.516
S3—Cd1—N5	75.10 (5)	C12—C11—H8	109.530
Cl4—Cd1—N5	96.09 (6)	H7—C11—H8	109.475
Cd1^{i}—Cl2—Cd1	93.70 (2)	C12—C11—H9	109.354
Cd1—S3—C8	101.41 (9)	H7—C11—H9	109.476
Cd1—N5—N7	120.12 (16)	H8—C11—H9	109.477
Cd1—N5—C12	131.48 (17)	C11—C12—C9	128.2 (2)
N7—N5—C12	106.5 (2)	C11—C12—N5	121.2 (2)
C8—N6—H1	119.986	C9—C12—N5	110.7 (2)
C8—N6—H2	120.013	C10—C13—H3	106.901
H1—N6—H2	120.001	C10—C13—H4	110.079
N5—N7—C8	118.6 (2)	H3—C13—H4	110.121
N5—N7—C10	109.9 (2)	C10—C13—H5	110.123
C8—N7—C10	131.4 (2)	H3—C13—H5	110.121
N7—C8—S3	122.18 (19)	H4—C13—H5	109.467
N7—C8—N6	117.9 (2)		

Symmetry code: (i) −*x*, −*y*, −*z*+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N6—H1···Cl4^{ii}	1.00	2.34	3.252 (3)	151
N6—H2···Cl4^{iii}	1.00	2.47	3.232 (3)	133

Symmetry codes: (ii) −*x*+1, −*y*, −*z*+2; (iii) *x*, *y*, *z*+1.