

The  $U_{ij}$  values of all the F atoms are large; attention has already been drawn (Halfpenny & Small, 1981) to this feature which prevails in all mercury(II) trifluoroacetate structures investigated. In this structure the nearest intermolecular contacts of the F atoms are to other F atoms; all separations are in excess of the van der Waals values.

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## Structure of the Adduct of Dimethyl Sulfoxide and 9-Methyladenine with Cadmium Chloride [*catena*-Di- $\mu$ -chloro-(dimethyl sulfoxide)(9-methyladenine)cadmium(II)]

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**Abstract.** C<sub>8</sub>H<sub>13</sub>CdCl<sub>2</sub>N<sub>5</sub>OS,  $M_r = 410.4$ , triclinic,  $P\bar{1}$ ,  $Z = 2$ ,  $a = 6.955$  (3),  $b = 8.774$  (3),  $c = 11.937$  (6) Å,  $\alpha = 97.69$  (3),  $\beta = 102.52$  (3),  $\gamma = 86.69$  (3)°,  $V = 704$  (1) Å<sup>3</sup>,  $D_x = 1.95$ ,  $D_m = 1.99$  (3) g cm<sup>-3</sup>,  $\lambda = 0.71073$  Å. Final  $R = 0.031$  for 5526 non-zero reflections. The structure consists of approximately octahedrally coordinated Cd<sup>2+</sup> species interconnected by chlorine bridges to form a one-dimensional polymer. The coordination polyhedron of the metal atom is made up of four Cl atoms, one O atom from dimethyl sulfoxide and an N atom, N(7), from the purine ring. The bonded distances are: Cd–Cl 2.611–2.653 (1); Cd–O 2.291 (2); Cd–N 2.357 (2) Å.

**Introduction.** <sup>113</sup>Cd NMR spectroscopy with a demonstrated chemical shift range of ~850 p.p.m. has been shown in recent years to offer potential as a sensitive probe of metal-ion sites in a variety of compounds, including proteins and enzymes (Rodesiler, Griffith, Ellis & Amma, 1980, and references therein). It is not clear whether Cd has a specific site preference in nucleotides thereby imposing a limit to its application as a probe of polynucleotides. For example, in purine nucleotides crystal-structure evidence indicates that

Cd<sup>2+</sup> binds to phosphate oxygen as well as purine bases to give a complicated three-dimensional structure (Goodgame, Jeeves, Reynolds & Skapski, 1975a; Clark & Orbell, 1975; Goodgame, Jeeves, Reynolds & Skapski, 1975b; Purnell, Estes & Hodgson, 1976). The Cd<sup>2+</sup> interaction with nucleic acid bases and nucleotides has been reviewed along with the interactions of other metal ions (Hodgson, 1977; Marzilli, 1977; Lippard, 1978; Marzilli & Kistenmacher, 1977; Gellert & Bau, 1979; Martin & Miriam, 1979; Swaminathan & Sundaralingam, 1979; Pezzano & Podo, 1980). We have demonstrated that a relatively simple complex can be formed from 6-mercaptapurine and CdCl<sub>2</sub>; Griffith & Amma (1979) have determined its crystal structure and observed its <sup>113</sup>Cd NMR at 554 p.p.m. deshielded from the Cd(ClO<sub>4</sub>)<sub>2</sub>-water standard. The present compound is another compound in this series. Unfortunately, it has very low solubility in NMR solvents and the <sup>113</sup>Cd NMR will have to be measured on solid samples. We report on the crystal structure at this time, and the structure-<sup>113</sup>Cd NMR correlation will be reported later.

To prepare the title compound, 0.03 g (0.002 mol) of 9-methyladenine (Cyclo Chemical) was dissolved in 30 ml of 1 M HCl and added to 0.43 g (0.002 mol) of CdCl<sub>2</sub>·2½ H<sub>2</sub>O (Baker & Adamson) dissolved in 20 ml

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of 1 M HCl, resulting in the immediate precipitation of a white powder. This powder was collected and dissolved with gentle heating in a dimethylformamide/dimethyl sulfoxide (1:2) solution, and diffraction-quality crystals of the title compound appeared over a period of two days. A single crystal  $\sim 0.36 \times 0.16 \times 0.52$  mm was mounted on a CAD-4 diffractometer interfaced to a PDP-11/40, the crystal was aligned and intensity data collected by standard techniques (Enraf-Nonius, 1980). Details are found in Table 1.

Table 1. *Unit-cell and data parameters*

Graphite monochromator,  $2\theta = 6.1^\circ$ ;  $\mu = 20.6 \text{ cm}^{-1}$ ; room temperature  $\sim 291 \text{ K}$ .  
 Faces of the form  $\{100\}\{010\}\{001\}$ .  
 Absorption corrections made and maximum and minimum transmission factors found were 0.686–0.487 (Frenz, 1980).  
 $P$  factor = 0.030 in  $\sigma(F_o^2) = [\sigma(I_{\text{raw}})^2 + (P \times I_{\text{raw}})^2]^{1/2}/LP$  and  $w = 1/\sigma(F_o)^2$ .  
 Data considered non-zero if  $F^2 > 4\sigma F^2$ .  
 6722 independent  $hkl$ 's measured in  $\omega$ - $2\theta$  mode.  
 5526 reflections used to solve and refine structure.  
 Variable scan speed with preliminary scan speed of  $4^\circ (2\theta) \text{ min}^{-1}$ .  
 25 reflections used in orientation matrix (checked every 24 h).  
 3 standard reflections monitored every 100 reflections, decay less than 1%.  
 Structure refined by full-matrix least squares, including anisotropic temperature factors and anomalous-dispersion corrections with weights based upon intensity statistics (Frenz, 1980).  
 Secondary-extinction coefficient =  $0.53 \times 10^{-6}$ .  
 Largest shift/error at end of refinement = 0.13.  
 Final least squares performed on Amdahl V6 (Stewart, 1979).  
 Number of variables = 163.  
 Final  $R = 0.031$ , weighted  $R = 0.065$ .  
 Error of observation of unit weight = 1.51.

Table 2. *Atomic coordinates and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

$$B_{\text{eq}} = \frac{3}{2}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	$x$	$y$	$z$	$B_{\text{eq}} (\text{\AA}^2)$
Cd	0.22447 (1)	0.01999 (1)	0.42759 (1)	1.948 (4)
Cl(1)	0.53549 (8)	-0.15388 (6)	0.39150 (5)	2.40 (2)
Cl(2)	-0.09359 (9)	0.17896 (6)	0.46349 (6)	2.80 (2)
S	0.3554 (1)	0.37580 (6)	0.38072 (5)	3.24 (3)
O	0.2951 (3)	0.2124 (2)	0.3320 (2)	3.29 (7)
N(1)	0.2764 (3)	-0.1233 (2)	-0.0274 (2)	2.64 (7)
N(3)	-0.0148 (3)	-0.2735 (2)	-0.0514 (2)	2.79 (7)
N(6)	0.4201 (3)	0.0231 (2)	0.1431 (2)	2.90 (7)
N(7)	0.0738 (3)	-0.0884 (2)	0.2397 (2)	2.28 (6)
N(9)	-0.1457 (3)	-0.2476 (2)	0.1234 (2)	2.32 (6)
C(2)	0.1318 (4)	-0.2198 (3)	-0.0872 (2)	2.88 (7)
C(4)	-0.0114 (3)	-0.2190 (2)	0.0601 (2)	2.11 (7)
C(5)	0.1243 (3)	-0.1198 (2)	0.1334 (2)	1.93 (6)
C(6)	0.2756 (3)	-0.0701 (2)	0.0838 (2)	2.14 (7)
C(8)	-0.0888 (3)	-0.1658 (3)	0.2296 (2)	2.39 (7)
C(9)	-0.3115 (4)	-0.3466 (3)	0.0837 (2)	3.52 (7)
C(10)	0.5217 (6)	0.4190 (3)	0.2970 (3)	4.9 (2)
C(11)	0.1489 (6)	0.4948 (4)	0.3242 (4)	5.7 (2)

The structure was solved by standard heavy-atom methods and refined as indicated in Table 1.\* The atomic coordinate parameters and errors are listed in Table 2. Selected interatomic distances and angles and errors are listed in Table 3. An ORTEP (Johnson, 1970) drawing of the immediate environment of the Cd atom is shown in Fig. 1.

**Discussion.** The structure may be described as a linear polymer made up of octahedrally coordinated Cd

\* Lists of structure factors, anisotropic thermal parameters and routine bond distances and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36474 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Bonded distances (Å) and angles (°) with e.s.d.'s in parentheses*

The routine distances and angles have been deposited.

Cd—Cd'	3.8646 (2)	Cd—O	2.291 (2)
Cd—Cd''	3.9358 (2)	Cd—N(7)	2.357 (2)
Cd—Cl(1)	2.6530 (6)	O—S	1.519 (2)
Cd—Cl(1')	2.6106 (5)	S—C(11)	1.790 (4)
Cd—Cl(2)	2.6300 (7)	S—C(10)	1.770 (4)
Cd—Cl(2'')	2.6213 (8)	N(7)—C(8)	1.328 (3)
Cl(1)—Cd—Cl(1')	85.52 (2)	Cl(2'')—Cd—N(7)	96.06 (5)
Cl(1)—Cd—Cl(2'')	94.41 (2)	Cl(2)—Cd—O	88.78 (5)
Cl(1)—Cd—Cl(2)	177.0 (3)	Cl(2)—Cd—N(7)	94.04 (5)
Cl(1)—Cd—O	93.87 (5)	O—Cd—N(7)	83.10 (7)
Cl(1)—Cd—N(7)	84.82 (4)	Cd—O—S	128.7 (1)
Cl(1')—Cd—Cl(2'')	96.18 (3)	Cd—Cl(1)—Cd'	94.48 (2)
Cl(1')—Cd—Cl(2)	96.15 (2)	Cd—Cl(2)—Cd''	97.09 (2)
Cl(1')—Cd—O	86.06 (4)	Cd—N(7)—C(8)	116.8 (2)
Cl(1')—Cd—N(7)	164.9 (1)	Cd—N(7)—C(5)	137.0 (1)
Cl(2)—Cd—Cl(2'')	82.91 (2)	O—S—C(11)	104.9 (1)
Cl(2'')—Cd—O	171.6 (1)	O—S—C(10)	104.2 (1)

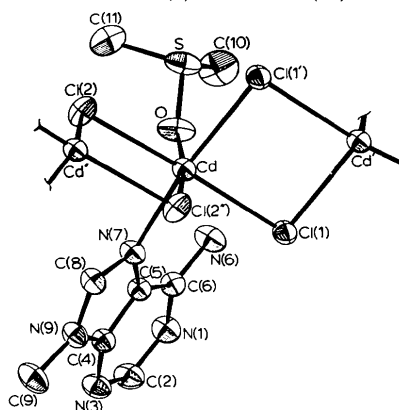



Fig. 1. An ORTEP (Johnson, 1970) drawing of the environment about the Cd atom also showing the propagation of the Cd atoms

to form the Cd—Cl—Cd chain. The notation is consistent with the tables and the primes refer to an inversion through the center of symmetry at  $\frac{1}{2}, 0, \frac{1}{2}$  [center of the Cd, Cl(1'), Cl(1), Cd' ring], the double prime refers to an inversion through the center of symmetry at  $0, 0, \frac{1}{2}$  [center of the Cd'', Cl(2), Cl(2''), Cd ring].

atoms sharing edges with adjacent octahedra, Fig. 1. The Cd octahedron for purposes of description may be considered as Cl(1), Cl(1'), Cl(2), N(7) as equatorial atoms and O and Cl(2'') as axial atoms. This sharing of edges is then described by considering Cl(1) and Cl(1') as equatorial atoms being shared with an adjacent octahedron and Cl(2) and Cl(2'') as equatorial and axial atoms being shared with a different adjacent octahedron, thus propagating the linear polymer. In this description of the Cd octahedron the N(7) of the purine ring would occupy the remaining equatorial site and the oxygen of the dimethyl sulfoxide the remaining axial site.

This mode of sharing of edges of the octahedron

leads to an alternation of Cd  Cd bridges such that

the adjacent bridges are perpendicular to one another. The purine ring is probably hydrogen bonded *via* N(6) to Cl(1) and the oxygen of the dimethyl sulfoxide. The N(6)—Cl(1) distance is 3.451 (8) Å with a concomitant C(6)—N(6)—Cl(1) angle of 97.89 (4)°. The N(6)—O distance is 2.879 (9) Å with a C(6)—N(6)—O angle of 110.74 (5)°. The dihedral angles between the normals of the purine ring, Cl(2)—Cd—Cl(2'') and Cl(1')—Cd—Cl(1), are 81.2 (1) and 54.5 (1)° respectively; that is the purine ring plane is essentially perpendicular to the Cl(2)—Cd—Cl(2'') bridge and canted to the Cl(1)—Cd—Cl(1') bridge. The latter is probably determined by the hydrogen bonding. The collection of the above facts may be used to describe the linear polymer as a ribbon with a lateral separation determined by van der Waals interactions between the dimethyl sulfoxide group and Cl(2) atoms thus creating an unusual packing for a metal—purine structure. In most metal—purine base structures, regardless of whether or not the base is blocked at N(9), the structure contains base stacking between the purine rings. In this case there are no base—base distances less than 4 Å. In addition, there seems to be no hydrogen bonding involving N(1) and N(3) of the purine ring system.

The bonding to the N(7) site of the purine ring is the expected coordination site when N(9) is blocked. The octahedron about Cd is somewhat distorted as the appropriate angles indicate, Table 3. The Cd—N distance is normal compared to previously observed values (Purnell *et al.*, 1976; Aoki, 1976; Wei & Jacobson, 1981). The Cd—Cl bridging distances are similar to those found in other Cd—Cl—Cd bridges (Griffith & Amma, 1979). The purine ring distances and angles are also normal and the expected values; see *e.g.* Sletten & Thorstensen (1974), Sletten & Ruud (1975).

Under the acid conditions of preparation it might seem surprising that the purine ring is not protonated.

However, there is ample precedence for such behavior; see *e.g.* Sletten & Thorstensen (1974) and Sletten & Ruud (1975). It is possible that the reaction pathway is through some protonated intermediates, but these do not remain as part of the final products.

The species described herein is not the only product of this reaction of CdCl<sub>2</sub> with 9-methyladenine. Small changes in pH of the reaction media yield a more soluble product more amenable to <sup>113</sup>Cd NMR solution studies. The structure analysis of this product is underway and the solid and the solution (where applicable) <sup>113</sup>Cd NMR of these reaction products will be reported in detail elsewhere.

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