

Details on the geometry of the anions and ligands are provided in the supplementary material. Phosphine coordination increases the C–P–C angles (mean 108.0°) compared with the free ligand (101.5°) (Allman, Goel & Beauchamp, 1986), as already pointed out (Makhija *et al.*, 1973). In the uncoordinated phosphine, the O–CH<sub>3</sub> bond is almost perfectly eclipsed with respect to the adjacent ring (C–C–O–C torsion 5°). In the present case, this orientation is observed for six of the nine independent aromatic rings, although the deviations reach 20° (supplementary material). On the other hand, ring number 8 shows a *gauche* orientation [67 (5)°]. For the two remaining rings (numbers 7 and 9), the methyl groups are involved in a twofold disorder ('open' atoms in Fig. 1). In both cases, one orientation is roughly eclipsed, the other is *gauche*. The mean ring–O and O–CH<sub>3</sub> distances are 1.357 (15) and 1.396 (15) Å, respectively, and the ring–O–CH<sub>3</sub> angle is 119.0 (9)°. Similar values were reported by Nyburg & Faerman (1986).

The perchlorate oxygens have high thermal motion, which leads to Cl–O distances [mean 1.322 (15) Å, range 1.296–1.371 Å,  $\sigma = 0.018$  Å (supplementary material)] artificially shorter than normal. They have the expected tetrahedral geometry (O–Cl–O angles ranging from 103.1 to 114.0°,  $\sigma = 0.9^\circ$ ).

Thanks are due to M. J. Olivier for collecting the X-ray data.

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## N(8)-Coordinating Allopurinol: Structure of Bis(allopurinol)diaquadichlorometal(II) (Metal = Co, Ni)

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(Received 12 February 1988; accepted 28 April 1988)

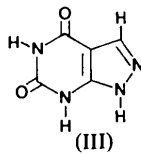
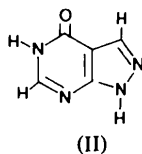
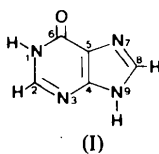
**Abstract.** [CoCl<sub>2</sub>(C<sub>5</sub>H<sub>4</sub>N<sub>4</sub>O)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>],  $M_r = 438.10$ , triclinic,  $P\bar{1}$ ,  $a = 6.459$  (2),  $b = 6.538$  (1),  $c =$

$9.631$  (1) Å,  $\alpha = 105.50$  (1),  $\beta = 96.60$  (2),  $\gamma = 105.56$  (2)°,  $V = 369.8$  (3) Å<sup>3</sup>,  $Z = 1$ ,  $D_x = 1.97$ ,  $D_m = 1.97$  g cm<sup>-3</sup>. [NiCl<sub>2</sub>(C<sub>5</sub>H<sub>4</sub>N<sub>4</sub>O)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>],  $M_r = 437.86$ , triclinic,  $P\bar{1}$ ,  $a = 6.438$  (4),  $b = 6.516$  (1),

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$c = 9.556(5) \text{ \AA}$ ,  $\alpha = 105.64(3)$ ,  $\beta = 97.08(4)$ ,  $\gamma = 105.59(4)^\circ$ ,  $V = 363.8(7) \text{ \AA}^3$ ,  $Z = 1$ ,  $D_x = 2.00 \text{ g cm}^{-3}$ ,  $F(000) = 222$ . The structure of  $\text{Co}(\text{C}_5\text{H}_4\text{N}_4\text{O})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$  was solved by Patterson synthesis using 4174 observed reflections and refined by full-matrix least-squares calculations. Mo  $K\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$ ,  $\mu = 14.69 \text{ cm}^{-1}$ ,  $F(000) = 221$ , room temperature,  $R = 0.027$ . The molecular structure of the octahedral complex is of the type  $[\text{CoCl}_2(\text{C}_5\text{H}_4\text{N}_4\text{O})_2(\text{H}_2\text{O})_2]$  including two N(8)-coordinated monodentate neutral allopurinol (pyrazolo[3,4-*d*]pyrimidin-6-one) ligands. The coordinated purine rings are stacked along the  $a$  axis with a minimum spacing distance of  $3.19 \text{ \AA}$ . Hydrogen-bonding contacts of the type  $\text{N}-\text{H}\cdots\text{Cl}$ ,  $\text{O}-\text{H}\cdots\text{Cl}$  and  $\text{O}-\text{H}\cdots\text{O}$  stabilize the layered structure. According to nearly identical crystal data, powder diffraction diagrams and thermogravimetric decomposition curves, the corresponding nickel complex  $[\text{NiCl}_2(\text{C}_5\text{H}_4\text{N}_4\text{O})_2(\text{H}_2\text{O})_2]$  is isostructural with its cobalt analogue.

**Introduction.** The antihyperuricemic drug allopurinol (pyrazolo[3,4-*d*]pyrimidin-6-one) (II), a potent inhibitor of the molybdenum and iron-containing enzyme xanthine oxidase, is used in the treatment of gout. Its naturally occurring isomer hypoxanthine (I) is formed by degradation of nucleic acids. Xanthine oxidase catalyzes the oxidation of hypoxanthine *via* xanthine to uric acid, which subsequently is released from the active site of the enzyme (Stiefel, 1977; Hille & Massey, 1985). Alloxanthine (pyrazolo[3,4-*d*]pyrimidine-2,6-dione) (III), however, the enzymatic oxidation product of the drug allopurinol, inactivates xanthine oxidase by irreversible coordination to the reduced form of the molybdenum centre of the enzyme. The production of uric acid, therefore, is inhibited (Hawkes, George & Bray, 1984), and patients receiving the drug allopurinol excrete much of their purine as xanthine. In this context, the coordination properties of allopurinol are of much current interest. Allopurinol is also used in conjunction with 6-mercaptopurine in the treatment of leukemia.



We recently reported on metal sulfato complexes of the type  $M^{II}(\text{allopurinol})_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$  ( $M = \text{Co}, \text{Ni}, \text{Zn}, \text{Cd}$ ), representing the first structurally characterized compounds involving allopurinol as an uncharged neutral ligand (Hänggi, Schmalle & Dubler, 1988). In these complexes, monodentate coordination of allopurinol to the metal atom through N(8) has been established.

As part of a programme elucidating the coordination properties of oxo- and thiopurines, we here describe the synthesis and structure of cobalt and nickel chloro complexes of neutral allopurinol.

**Experimental.**  $\text{Co}(\text{allopurinol})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$  was prepared by adding a solution of  $3.0 \text{ g}$  ( $12.6 \text{ mmol}$ )  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  in  $10 \text{ ml H}_2\text{O}$  to  $100 \text{ mg}$  ( $0.73 \text{ mmol}$ ) allopurinol dissolved in  $10 \text{ ml H}_2\text{O}$ . The reaction mixture was heated and kept for crystallization at  $348 \text{ K}$ . After two weeks, crystals of composition calculated as  $\text{C } 27.42, \text{H } 2.76, \text{N } 25.58, \text{Cl } 16.19, \text{H}_2\text{O } 8.22\%$  and observed as  $\text{C } 27.40, \text{H } 2.68, \text{N } 25.70, \text{Cl } 16.20, \text{H}_2\text{O } 8.63\%$  (thermogravimetric analysis) could be isolated.

$\text{Ni}(\text{allopurinol})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$  was synthesized by heating a solution of  $100 \text{ mg}$  ( $0.73 \text{ mmol}$ ) allopurinol and  $3.0 \text{ g}$  ( $12.6 \text{ mmol}$ )  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  in  $20 \text{ ml H}_2\text{O}$ . The solution was kept for crystallization at  $348 \text{ K}$ . Ten days later, green crystals were formed. The composition was calculated as  $\text{C } 27.43, \text{H } 2.76, \text{N } 25.59, \text{Cl } 16.19, \text{H}_2\text{O } 8.23\%$  and observed as  $\text{C } 27.49, \text{H } 2.78, \text{N } 25.79, \text{Cl } 16.14, \text{H}_2\text{O } 11.50\%$ . The pH value of the reaction solutions, measured with a pH glass electrode (Methrom), was  $3.5$  (Co complex) and  $3.0$  (Ni complex) respectively.

Thermogravimetric data were recorded on a Perkin-Elmer TGS-2 thermobalance in flowing oxygen atmosphere. The two complexes show similar degradation behaviour, supporting the suggestion of an isomorphous structural relationship. The thermal decomposition occurs in two steps; a dehydration reaction in the temperature range of  $470\text{--}520 \text{ K}$  (Co) and  $490\text{--}590 \text{ K}$  (Ni), followed by a decomposition to  $\text{Co}_3\text{O}_4$  and  $\text{NiO}$  respectively. The anhydrous cobalt complex is stable in the temperature range from  $520$  to  $650 \text{ K}$ , whereas the plateau of the thermogravimetric curve corresponding to the anhydrous nickel complex is not well defined. Therefore, the observed weight loss in the first decomposition step of about  $11.5\%$ , attributed to dehydration, may already include some weight loss due to decomposition of the allopurinol ligand.

A crystal of the cobalt complex with dimensions  $0.27 \times 0.29 \times 0.39 \text{ mm}$  was selected for X-ray investigations. The lattice constants of both complexes were obtained from least-squares refinement of 25 reflections in the interval  $17 < \theta < 20^\circ$  on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromatized Mo  $K\alpha$  radiation. Intensities of 9150 reflections (excluding standards) in the interval  $1 < \theta < 40^\circ$  were collected using the  $\omega$ - $2\theta$  scan technique with variable scan speeds between  $2.9$  and  $10.0 \text{ min}^{-1}$ . The index range was  $-11 \leq h \leq 11, -11 \leq k \leq 11, -17 \leq l \leq 17$ . Six standard reflections monitored every 2 h of measuring time showed less than  $0.6\%$  loss of intensities. Orientation was controlled every 250 reflections using five standard reflections. Data reduction ( $R_{\text{int}} = 0.013$ ) led to 4575 unique reflections. The data were corrected

Table 1. *Positional parameters of*  
Co(allopurinol)<sub>2</sub>Cl<sub>2</sub>·2H<sub>2</sub>O

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

	x	y	z	$U_{eq}^*/U_{iso}(\text{\AA}^2)$
Co	0.5000	0.0000	0.5000	0.0156 (1)
O(1)	0.2462 (1)	0.2141 (1)	0.4565 (1)	0.0284 (1)
O(1)	0.2467 (1)	-0.2202 (1)	0.5525 (1)	0.0297 (1)
N(1)	0.8234 (1)	0.6733 (1)	1.1822 (1)	0.0230 (1)
C(2)	0.8480 (1)	0.8230 (1)	1.1045 (1)	0.0239 (2)
N(3)	0.8084 (1)	0.7715 (1)	0.9624 (1)	0.0228 (1)
C(4)	0.7391 (1)	0.5466 (1)	0.8944 (1)	0.0172 (1)
C(5)	0.7122 (1)	0.3797 (1)	0.9617 (1)	0.0174 (1)
C(6)	0.7550 (1)	0.4423 (1)	1.1191 (1)	0.0205 (2)
O(6)	0.7356 (1)	0.3172 (1)	1.1944 (1)	0.0373 (2)
C(7)	0.6380 (1)	0.1768 (1)	0.8456 (1)	0.0198 (1)
N(8)	0.6195 (1)	0.2174 (1)	0.7182 (1)	0.0192 (1)
N(9)	0.6819 (1)	0.4441 (1)	0.7486 (1)	0.0200 (1)
H(1)	0.835 (3)	0.712 (3)	1.276 (2)	0.033 (5)
H(2)	0.893 (3)	0.985 (3)	1.168 (2)	0.027 (4)
H(7)	0.600 (2)	0.030 (2)	0.847 (1)	0.013 (3)
H(9)	0.683 (3)	0.484 (3)	0.676 (2)	0.032 (5)
H(11)	0.117 (4)	-0.201 (4)	0.544 (2)	0.061 (7)
H(12)	0.275 (5)	-0.314 (5)	0.613 (3)	0.116 (11)

\* The standard deviations of the  $U_{eq}$ 's have been calculated after Schomaker & Marsh (1983).

for Lorentz and polarization effects, and an absorption correction, based on ten crystal faces, was applied (min. and max. transmission factors are 0.64 and 0.72 respectively).

The structure was solved by Patterson synthesis with *SHELXS86* (Sheldrick, 1985) and refined with *SHELX76* (Sheldrick, 1976). After anisotropic refinement of the non-hydrogen atoms, using 4174 reflections with  $I \geq 3\sigma(I)$ , all H atoms could be localized in the difference Fourier maps and were included in the refinement with free positional and free isotropic temperature factors. Six reflections were omitted because secondary extinction was suspected. Final refinement of 139 parameters, using 4168 observed reflections and minimizing  $\sum w(|F_o| - |F_c|)^2$  with  $w^{-1} = \sigma^2(F_o)$ , converged to  $R = 0.027$  and  $wR = 0.035$ . The maximum final shift-to-e.s.d. ratio  $\Delta/\sigma$  was 0.063 (H-atom parameter). Maximum and minimum electron densities in final difference Fourier synthesis were  $0.53 \text{ e \AA}^{-3}$ , located between C(7) and N(8), and  $-0.88 \text{ e \AA}^{-3}$ , located at a distance of 0.37 Å from the Cl atom. Atomic scattering factors were those of *SHELX*.

The refined atomic parameters are listed in Table 1.\*

**Discussion.** The molecular structure of the cobalt complex is of the type [CoCl<sub>2</sub>(C<sub>5</sub>H<sub>4</sub>N<sub>4</sub>O)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>],

\* Lists of structure factors and anisotropic thermal parameters, X-ray powder diffraction data of Co(allopurinol)<sub>2</sub>Cl<sub>2</sub>·2H<sub>2</sub>O and Ni(allopurinol)<sub>2</sub>Cl<sub>2</sub>·2H<sub>2</sub>O and bonding distances and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44995 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester, CH1 2HU, England.

shown in Fig. 1. The Co ion exhibits a slightly distorted octahedral geometry with two monodentate allopurinol ligands coordinating *via* their N(8) atoms and two Cl ions, all in the equatorial plane; the axial positions are occupied by two water molecules. Bond lengths and angles are listed in Table 2. The Co—N distance of 2.115 (1) Å found in the title compound compares well with corresponding distances in other octahedral cobalt(II)—purine complexes. Reported values are, for example, 2.119 (1) Å in Co(hypoxanthine)SO<sub>4</sub>·5H<sub>2</sub>O (Dubler, Hänggi & Bensch, 1987), 2.128 (1) and 2.151 (1) Å in Co(allopurinol)<sub>2</sub>SO<sub>4</sub>·4H<sub>2</sub>O (Hänggi, Schmale & Dubler, 1988) and 2.16 (1) Å in Co(inosine 5'-monophosphate)·7H<sub>2</sub>O (Aoki, 1975). The distortion of the octahedral arrangement around the metal ion is evidenced by the angles N(8)—Co—O(1) [94.7 (1)°], N(8)—Co—Cl [90.2 (1)°] and O(1)—Co—Cl [88.9 (1)°]. On the basis of nearly identical unit cells, coinciding X-ray powder diffraction diagrams\* and similar thermogravimetric decomposition curves, the nickel complex is considered to be isostructural with its respective cobalt compound.

In the neutral free base allopurinol, H atoms are bonded to N(1) and N(9), but not to N(8) (Prusiner &

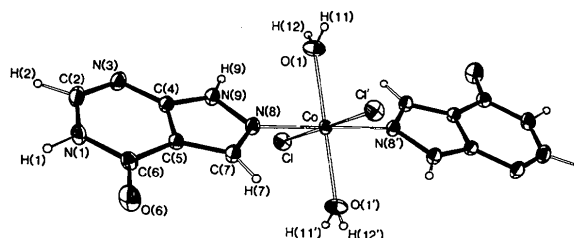


Fig. 1. ORTEP drawing (Johnson, 1965) of the coordination polyhedron of Co(allopurinol)<sub>2</sub>Cl<sub>2</sub>·2H<sub>2</sub>O.

Table 2. *Interatomic bond distances (Å) and angles (°) of* Co(allopurinol)<sub>2</sub>Cl<sub>2</sub>·2H<sub>2</sub>O

Co—N(8)	2.115 (1)		
Co—O(1)	2.078 (1)		
Co—Cl	2.492 (1)		
N(1)—C(2)	1.371 (2)	C(5)—C(7)	1.408 (1)
C(2)—N(3)	1.296 (1)	C(7)—N(8)	1.322 (1)
N(3)—C(4)	1.362 (1)	N(8)—N(9)	1.366 (1)
C(4)—C(5)	1.394 (1)	N(9)—C(4)	1.343 (1)
C(5)—C(6)	1.433 (1)	C(6)—O(6)	1.223 (1)
C(6)—N(1)	1.391 (1)		
N(8)—Co—O(1)	94.7 (1)	Co—N(8)—C(7)	131.4 (1)
N(8)—Co—Cl	90.2 (1)	Co—N(8)—N(9)	121.4 (1)
O(1)—Co—Cl	88.9 (1)		
C(6)—N(1)—C(2)	124.6 (1)	C(7)—N(8)—N(9)	107.1 (1)
N(1)—C(2)—N(3)	125.4 (1)	N(8)—N(9)—C(4)	110.7 (1)
C(2)—N(3)—C(4)	112.6 (1)	N(9)—C(4)—C(5)	107.0 (1)
N(3)—C(4)—C(5)	127.0 (1)	N(3)—C(4)—N(9)	126.0 (1)
C(4)—C(5)—C(6)	119.0 (1)	C(6)—C(5)—C(7)	135.6 (1)
C(5)—C(6)—N(1)	111.4 (1)	N(1)—C(6)—O(6)	121.5 (1)
C(4)—C(5)—C(7)	105.4 (1)	C(5)—C(6)—O(6)	127.1 (1)
C(5)—C(7)—N(8)	109.8 (1)		

\* See deposition footnote.

Sundaralingam, 1972). In analogy to the structures of  $M^{II}(\text{allopurinol})_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$  with  $M = \text{Co}, \text{Ni}, \text{Zn}$  or  $\text{Cd}$  (Hänggi, Schmale & Dubler, 1988), allopurinol is monodentately coordinating through N(8) in  $\text{Co}(\text{allopurinol})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ . Therefore N(8), the nitrogen atom, which is *not bonded* to an H atom in the neutral free base, seems to be a preferred coordination site for unsubstituted neutral allopurinol. This observation is contrary to the concept formulated by Hodgson (1977) that for unsubstituted purines the most probable site of coordination is the imidazole N atom which is *bonded* to an H atom in the free neutral ligand.

The results of structure analyses of metal complexes of ionic unsubstituted allopurinol give no evidence for N(8) metalation. Under acidic conditions, the N(8)-protonated allopurinolium cation is coordinating through N(9) in the Cl-bridged polymeric chain structure of  $\text{Cu}^{II}(\text{allopurinol}^+)\text{Cl}_3$  (Sheldrick & Bell, 1987a). Again, compared with the uncomplexed allopurinolium cation in the crystal structure of allopurinolium chloride (Sheldrick & Bell, 1987b), where N(1), N(3) and N(8) but not N(9) are bonded to H atoms, metalation occurs at the N atom of the five-membered ring which is not bonded to any H atom, *i.e.* N(9). Twofold negatively charged allopurinol, where all the ring N atoms are deprotonated, is coordinating through N(1) and N(9) in  $[(\text{CH}_3\text{Hg})_2(\text{allopurinol}^{2-})] \cdot 2\text{H}_2\text{O}$  (Sheldrick & Bell, 1987b). In complexes of neutral 9- $\text{CH}_3$ -allopurinol, finally, where N(9) is blocked, N(8) has also been established as the binding site in the structure of  $\text{Cu}^{II}(9\text{-CH}_3\text{-allopurinol})(\text{H}_2\text{O})\text{Cl}_2$  (Sheldrick & Bell, 1987a).

The molecular dimensions of the allopurinol ligand in the cobalt chloro complex described here are in close agreement with those of the sulfato complexes mentioned above. Most purine derivatives show significant alterations of the ring geometry, resulting from protonation (the term 'protonation' in this context is generally used to indicate that an H atom is bonded to the corresponding N atom, but does not necessarily mean that a cationic molecule is formed). Taylor & Kennard (1982) have reviewed the effects of protonation on the ring dimensions of different purine

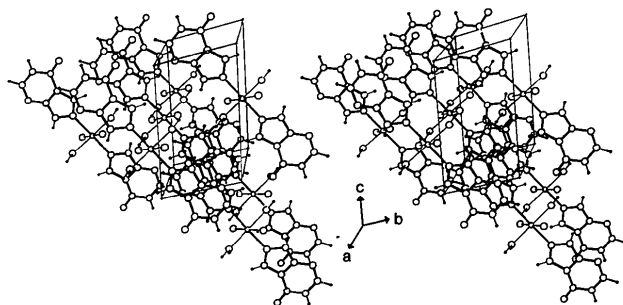


Fig. 2. ORTEP drawing (Johnson, 1965) of the packing diagram of  $\text{Co}(\text{allopurinol})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ .

Table 3. *Hydrogen-bonded contacts of  $\text{Co}(\text{allopurinol})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$*

$X\text{-H}\cdots Y$	$X\text{-H}$ (Å)	$\text{H}\cdots Y$ (Å)	$X\cdots Y$ (Å)	$X\text{-H}\cdots Y$ ( $^\circ$ )
N(1)-H(1) $\cdots$ Cl	0.86 (2)	2.64 (2)	3.467 (1)	164 (1)
N(9)-H(9) $\cdots$ Cl	0.81 (2)	2.59 (2)	3.335 (1)	153 (1)
N(9)-H(9) $\cdots$ O(1)	0.81 (2)	2.58 (2)	3.027 (1)	116 (2)
O(1)-H(11) $\cdots$ Cl	0.88 (2)	2.32 (3)	3.186 (2)	167 (2)
O(1)-H(12) $\cdots$ O(6)	0.99 (3)	1.87 (3)	2.676 (2)	137 (3)

bases. The major influence observed is an increase of the corresponding C-N-C angle of about  $4^\circ$  upon protonation of the N atom. Metalation instead of protonation can induce similar but much smaller changes of ring dimensions (Dubler, Hänggi & Schmale, 1987). A comparison of the geometry of neutral allopurinol (Prusiner & Sundaralingam, 1972), where N(1) and N(9) are protonated, with the corresponding values in  $\text{Co}(\text{allopurinol})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ , where N(1) and N(9) are protonated and N(8) is coordinating, may also be indicative of a very small influence of metalation on the ring geometry of allopurinol. The angle C(7)-N(8)-N(9) is  $106.4$  (3) in neutral allopurinol and  $107.1$  (1) $^\circ$  in the cobalt complex. The purine ring in  $\text{Co}(\text{allopurinol})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$  is approximately planar with a maximum deviation of  $0.017$  Å of the atom C(5) from the least-squares plane calculated through the nine ring atoms. The extraannular oxygen atom O(6) lies  $0.026$  Å below this purine plane.

The packing diagram is presented in Fig. 2. A stacking pattern of type II (Bugg, 1972), where the bases are stacked on top of each other rotated by about  $180^\circ$ , is observed. The purine rings, stacked along the *a* axis and related by a centre of inversion, form infinite sheets of bases parallel to the *bc* plane. The shortest stacking distance, calculated as the mean distance of all atoms of one molecule from the least-squares plane through the stacking molecule, is  $3.19$  Å.

Hydrogen-bonding distances and angles are listed in Table 3. There are no intermolecular hydrogen bonds between the allopurinol molecules, but the chloride ion participates in two hydrogen-bonding contacts of the type N-H $\cdots$ Cl and one contact of the type O-H $\cdots$ Cl. H(9), in addition, is involved in an 'intramolecular' hydrogen bond N(9)-H(9) $\cdots$ O(1), thus leading to a bifurcated hydrogen bond system around H(9). A relatively strong hydrogen bond with a donor-acceptor distance of  $2.676$  (2) Å is observed between the coordinated water molecule O(1) and the exocyclic oxygen atom O(6) of allopurinol.

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*Acta Cryst.* (1988). C44, 1564–1567

### *trans*-Diaquatetrakis(pyrazole)manganese(II) Dinitrate–Pyrazole (1/2)

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(Received 6 July 1987; accepted 19 May 1988)

**Abstract.** [Mn(C<sub>5</sub>H<sub>4</sub>N<sub>4</sub>O)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>·2C<sub>5</sub>H<sub>4</sub>N<sub>2</sub>, *M*<sub>r</sub> = 623.45, triclinic, *P* $\bar{1}$ , *a* = 9.150 (2), *b* = 9.449 (4), *c* = 9.583 (4) Å,  $\alpha$  = 79.75 (4),  $\beta$  = 87.83 (3),  $\gamma$  = 65.33 (3)°, *V* = 740.2 (5) Å<sup>3</sup>, *Z* = 1, *D*<sub>m</sub> = 1.40 (2), *D*<sub>x</sub> = 1.44 g cm<sup>-3</sup>,  $\lambda$ (Mo *K*α) = 0.71069 Å,  $\mu$  = 5.4 cm<sup>-1</sup>, *F*(000) = 323, *T* = 296 (2) K. Final *R* = 0.045 for 2538 observed unique reflections with *I* > 3σ(*I*). The structure consists of centrosymmetric complex units in which the central Mn<sup>II</sup> ion is in an octahedral arrangement. Two coordinated pyrazole molecules occupy the equatorial sites at distances of 2.245 (4) and 2.264 (3) Å, respectively, and the apical sites are occupied by coordinated water molecules at distances of 2.148 (3) Å. The asymmetric unit contains a further uncoordinated pyrazole molecule and a nitrate anion. The structure is formed from layers extending along the *ab* plane. The layer is held together primarily through hydrogen bonds involving the uncoordinated pyrazoles and nitrate ions approximately in the [100] and [110] directions. In the *c* direction the layers are held together through weak van der Waals forces and loose stacking of parallel pyrazole rings, especially in the [011] direction.

**Introduction.** Several manganese(II) complexes of pyrazole and its derivatives are reported to have been prepared and studied by different physical methods (Trofimenko, 1972), but the crystal structures of only three pyrazole complexes have been fully described (Reedijk, Stork-Blaisse & Verschoor, 1971; Gorter, van Ingen Schenau & Verschoor, 1974; Lumme,

Mutikainen & Lindell, 1983). Recently we prepared the crystals of the title compound and its crystal structure is described in this paper. The compound was also studied with respect to IR and reflectance spectra (Lumme, Lindell & Kivimäki, 1988) and thermal behaviour (Lumme, 1985).

**Experimental.** Colourless prism, approximately 0.20 × 0.35 × 0.63 mm, obtained by recrystallization from a hot aqueous solution was sealed into a capillary tube (Lindemann glass) in its mother liquor for data collection. Weissenberg photographs established the crystal system as triclinic. The space group *P* $\bar{1}$  was assigned on the basis of the composition and the complete structure analysis. The unit-cell parameters were determined by least-squares treatment of the adjusted angular settings of 21 reflections, 6.67 ≤  $\theta$  ≤ 23.80°, measured on a Nicolet P3F diffractometer. The intensity measurements were carried out at room temperature [296 (2) K] with graphite-monochromated Mo *K*α radiation and the ω–2θ scan technique. The scan rate varied from 1.5 to 29.3° min<sup>-1</sup>, depending on the number of counts measured in a fast preliminary scan through the peak. A set of 3397 unique reflections was obtained from the 3612 reflections measured up to the maximum value of 2θ = 55°, the minimum being 3° (*h*: 0, 12; *k*: –13, 13; *l*: –13, 13). 2538 reflections with *I* > 3σ(*I*) were considered as observed and used in the refinement which was based on *F*. Two strong reflections monitored periodically after each group of 48 reflections exhibited no significant variation of intensity. The intensities were corrected for Lorentz and polarization effects and empirically for absorption on

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