the trend for the line to have zero intercept, we suggest that equation (I), from which (III) is derived, is the more appropriate expression for determining bond valence values from bond length data.

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N(8)-Coordinating Allopurinol: Structure of Bis(allopurinol)triaqua(sulfato)copper(II) Hydrate

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Abstract. $[Cu(SO_4)(C_5H_4N_4O)_2(H_2O)_3].H_2O$, $M_r = 503.89$, triclinic, $P\bar{1}$, $a = 8.286$ (2), $b = 9.836$ (5), $c = 10.860$ (3) Å, $\alpha = 96.68$ (4), $\beta = 91.95$ (2), $\gamma = 94.41$ (3)°, $V = 875.7$ (10) Å^3, $Z = 2$, $D_x = 1.911$, $D_m = 1.92$ g cm^{-3}, $\mu = 14.36$ cm^{-1}, $F(000) = 514$, Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å), $T = 296$ K. The

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structure was determined by single-crystal X-ray diffraction using 10 806 independent reflections and refined by full-matrix least-squares calculations with 7446 reflections with $I \geq 3\sigma(I)$ to $R = 0.033$. The complex is monomeric; its $(4 + 2)$-distorted octahedral structure is of the type $[Cu^{II}(SO_4)(C_5H_4N_4O)_2$-$(H_2O)_3].H_2O$ including two N(8)-coordinating monodentate neutral allopurinol ligands. The bonding distances within the equatorial plane are Cu—N(8) 2·002 (1) and 2·012 (1) Å, respectively, Cu—O_{H_2O} 2·008 (1) Å and Cu—O_{SO_4} 2·033 (1) Å, whereas the two axial distances Cu—O_{H_2O} are 2·290 (1) and 2·306 (1) Å. The noncoordinating water molecules are linked via hydrogen-bonding contacts of the type O—H···O with the complex unit. The coordinated purine rings are stacked, rotated about 180° with respect to each other with a mean spacing of 3·26 Å.
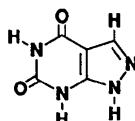
Introduction. Hypoxanthine (I), the naturally occurring isomer of allopurinol (II) (pyrazolo[3,4-d]-pyrimidin-6-one) is formed by degradation of nucleic acids. The molybdenum- and iron-containing enzyme xanthine oxidase catalyses the oxidation of hypoxanthine via xanthine to uric acid, which is subsequently released from the active site of the enzyme (Stiefel, 1977; Hille & Massey, 1985). In the case of metabolic defects, the uric acid level may be increased and sodium hydrogenurate crystals are deposited in joints. This disease, known as gout, is clinically treated by the antihyperuricemic drug allopurinol, which is also a substrate for xanthine oxidase. Alloxanthine (III) (pyrazolo[3,4-d]pyrimidine-2,6-dione), 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.
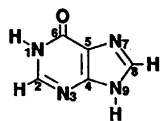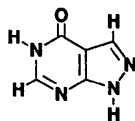
Hypoxanthine (I)   Allopurinol (II)   Alloxanthine (III)

In this context, the interaction of metal ions with allopurinol has been examined in order to provide structural information concerning the metal binding site of this purine derivative. Complexes involving neutral unsubstituted allopurinol are of the type $[M^{II}(SO_4)(C_5H_4N_4O)_2(H_2O)_3].H_2O$ with M = Co, Ni, Zn, Cd (Hänggi, Schmalle & Dubler, 1988a), $[M^{II}Cl_2(C_5H_4N_4O)_2(H_2O)_2]$ with M = Co, Ni (Hänggi, Schmalle & Dubler, 1988b) and Rh^{I}Cl-(allopurinol)(CO)₂.CH₃OH (Sheldrick & Günther,

1988). In all these complexes, with the sole exception of the rhodium complex, where metallation occurs at N(9), monodentate metal coordination of neutral allopurinol through N(8) is observed. In an effort to elucidate accurately the geometry of further metal allopurinol complexes, the structure determination of $[Cu^{II}(SO_4)(C_5H_4N_4O)_2(H_2O)_3].H_2O$ was performed.

Experimental. Single crystals of Cu(allopurinol)₂-SO₄.4H₂O were prepared by adding a solution of 3·0 g (12·0 mmol) CuSO₄.5H₂O in 10 ml 0.5 N H₂SO₄ to 100 mg (0·73 mmol) allopurinol dissolved in 10 ml 0·5 N H₂SO₄. The reaction mixture was heated to boiling and then kept for crystallization at 313 K. After one week, blue crystals of the composition calculated as C 23·84, H 3·20, N 22·24, S 6·36, H₂O 14·30% and observed as C 23·85, H 3·29, N 22·06, S6·51, H₂O 14·52% (thermogravimetric analysis) could be isolated. The density of the crystals (1·92 g cm⁻³, measured by flotation in CHCl₃/CH₂I₂) is in excellent agreement with the calculated value of 1·911 g cm⁻³.

Thermogravimetric data were recorded on a Perkin–Elmer thermobalance TGS-2 in a flowing oxygen atmosphere. The thermal degradation curve (Fig. 1) of this complex shows three well defined steps. Dehydration, occurring in a two-step reaction in the temperature range 353–513 K, is followed by complete decomposition to Cu₂O and subsequently to CuO. The decrease in weight of 11·2% of the first step of the dehydration reaction is in agreement with the calculated value for three water molecules (10·7%). The second step with a weight loss of 3·3% corresponds to the release of the last water molecule. In view of the structure of the complex involving three coordinating and one noncoordinating water molecule (see Fig. 2), this two-step dehydration reaction could be interpreted as follows: the first step corresponds to the elimination of the noncoordinating water molecule and of the two more weakly bonded water molecules in the apical positions of the $(4 + 2)$-Jahn–Teller-distorted copper coordination octahedron. This would imply an intermediate structure in which copper exhibits a square-planar coordination. The second step corresponds to the release of the remaining, firmly bonded water molecule in the equatorial plane of the coordination octahedron. The complete decomposition of Cu(allopurinol)₂SO₄ occurs in the temperature range 523–713 K with a sharp increase in the reaction rate at about 703 K. The X-ray powder diffraction data of the final product correspond to the values given for Cu₂O and CuO (Powder Diffraction File, 1969).

A single crystal of dimensions 0·12 × 0·75 × 0·40 mm was used for X-ray investigations on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromatized Mo $K\alpha$ radiation (λ =

0·71073 Å). Final cell parameters were obtained from least-squares refinement of 25 reflections in the interval $13 < \theta < 20°$. The intensities of 11 220 reflections (excluding standards) were recorded in the interval $1 < \theta < 40°$ using the $\omega–2\theta$ scan technique with a scan width $\Delta\omega = (0·90 + 0·35\tan\theta)°$ and a scan speed rate varied between 1·5 and 8·2° min^{-1}. The maximum counting time was 60 s. The index range was $-15 \le h \le 15$, $-17 \le k \le 17$, $0 \le l \le 19$. Standard deviations of intensities were derived from counting statistics using the measurement procedure of the Enraf–Nonius CAD-4 operator's guide (Enraf–Nonius, 1984). 50% of the 96 steps of an intensity profile were used for the left and right background measurement. Four standard reflections monitored every 3 h during data collection showed a mean total loss of intensities of 0·8%. To control orientation four standard reflections were collected every 250
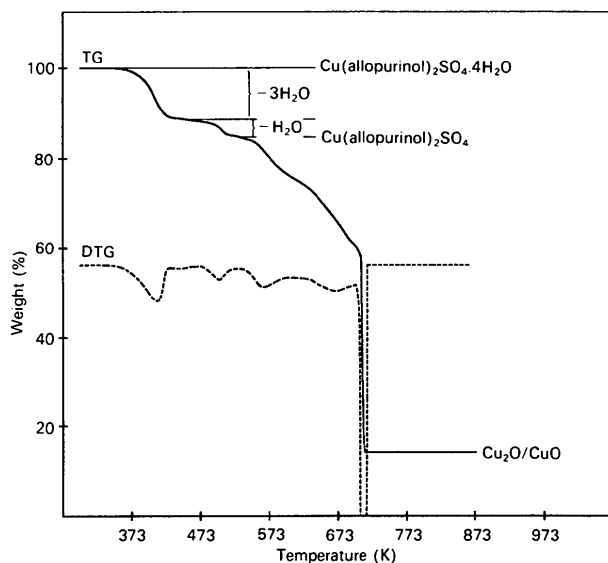

Fig. 1. Thermogravimetric (TG) and differential thermogravimetric (DTG) curves of the thermal degradation of Cu(allopurinol)₂SO₄.4H₂O.

Fig. 2. ORTEP drawing of the coordination polyhedron of Cu(allopurinol)₂SO₄.4H₂O.

reflections. Data reduction led to 10 806 unique reflections ($R_{int} = 0·0188$). The data were corrected for Lorentz and polarization effects, and an absorption correction, based on 12 crystal faces, was applied (min. and max. transmission factors 0·63 and 0·88, respectively). 1397 of a total of 3557 unobserved reflections with $I < 3\sigma(I)$ had negative intensities and 856 reflections were lower than $0·5\sigma(I)$. Arbitrary intensities of $I = 0·25\sigma(I)$ were attributed to both groups of reflections.

On the basis of similar unit cells and powder diffraction diagrams, the copper complex [Cu^{II}-(SO₄)(C₅H₄N₄O)₂(H₂O)₃].H₂O was considered to be isostructural with the corresponding sulfato complexes mentioned above. Therefore the structure determination was started with the atomic coordinates of the non-H atoms of the cadmium analogue (Hänggi, Schmalle & Dubler, 1988a). Anisotropic refinements were carried out with 7449 reflections with $I \ge 3\sigma(I)$ by minimizing $\sum w(|F_o| - |F_c|)^2$ with $w = K/\sigma^2(F_o)$ ($K = 1·44$) using SHELX76 (Sheldrick, 1976). All H atoms could be localized in subsequent difference Fourier maps and were included in the refinement with variable positonal and isotropic temperature factors. Three strong reflections were omitted because secondary extinction was suspected. The final refinement using 7446 observed reflections and 335 parameters converged with a maximum final shift/e.s.d. ratio of 0·06 to the discrepancy factors $R = 0·033$ and $wR = 0·033$. Including all unobserved reflections, the corresponding values are $R = 0·057$ and $wR = 0·037$ for 10 806 unique data. The standard deviation of an observation of unit weight S is 5·21. Maximum and minimum electron densities in final difference Fourier synthesis were 2·03 e Å^{-3}, located 1·92 Å from O(11) and $-0·82$ e Å^{-3}, located at a distance of 0·42 Å from the Cu atom. Atomic scattering factors for the neutral atoms and anomalous-dispersion terms for C, H, N, O and S atoms were those in SHELX76, and for Cu they were taken from International Tables for X-ray Crystallography (1974, Vol. IV). All calculations were performed on an HDSAS/XL V60 and a PDP 11/34 computer.

The refined atomic and isotropic thermal parameters are listed in Table 1.*

Discussion. The composition of the asymmetric unit of the complex, illustrated in Fig. 2, may be represented by the formula [Cu^{II}(SO₄)(C₅H₄N₄O)₂-(H₂O)₃].H₂O. The copper ion exhibits a distorted

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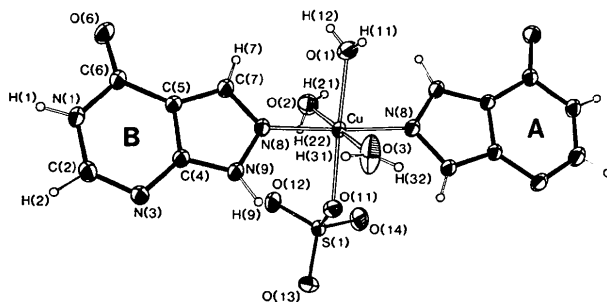
* Lists of structure factors, anisotropic thermal parameters and bond distances and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53972 (58 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional and thermal parameters of* $Cu(allopurinol)_2SO_4.4H_2O$

$$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}/U_{iso}(Å^2)
Cu	0·20196 (2)	0·03283 (2)	0·27246 (2)	0·01813 (3)
S(1)	−0·17491 (4)	−0·01056 (3)	0·24912 (3)	0·01876 (4)
O(11)	−0·0229 (1)	−0·0318 (1)	0·3223 (1)	0·0225 (2)
O(12)	−0·1731 (1)	0·1356 (1)	0·2304 (1)	0·0279 (2)
O(13)	−0·3136 (1)	−0·0468 (1)	0·3247 (1)	0·0267 (2)
O(14)	−0·1843 (2)	−0·0985 (1)	0·1317 (1)	0·0340 (3)
N(1A)	0·3346 (2)	−0·5129 (1)	−0·0877 (2)	0·0228 (2)
C(2A)	0·2360 (2)	−0·5676 (2)	−0·0055 (2)	0·0273 (3)
N(3A)	0·1673 (2)	−0·4985 (1)	0·0854 (1)	0·0279 (3)
C(4A)	0·2060 (2)	−0·3607 (1)	0·0899 (1)	0·0198 (2)
C(5A)	0·3044 (2)	−0·2936 (1)	0·0109 (1)	0·0189 (2)
C(6A)	0·3789 (2)	−0·3742 (1)	−0·0864 (1)	0·0201 (2)
O(6A)	0·4716 (1)	−0·3349 (1)	−0·1638 (1)	0·0297 (2)
C(7A)	0·3079 (2)	−0·1539 (1)	0·0562 (1)	0·0228 (2)
N(8A)	0·2191 (2)	−0·1376 (1)	0·1550 (1)	0·0214 (2)
N(9A)	0·1554 (2)	−0·2646 (1)	0·1748 (1)	0·0227 (2)
N(1B)	0·1811 (2)	0·6068 (1)	0·6307 (1)	0·0228 (2)
C(2B)	0·0875 (2)	0·5207 (1)	0·6927 (1)	0·0224 (3)
N(3B)	0·0559 (2)	0·3890 (1)	0·6603 (1)	0·0223 (2)
C(4B)	0·1273 (2)	0·3444 (1)	0·5531 (1)	0·0182 (2)
C(5B)	0·2247 (2)	0·4230 (1)	0·4817 (1)	0·0192 (2)
C(6B)	0·2587 (2)	0·5666 (1)	0·5225 (1)	0·0230 (3)
O(6B)	0·3424 (2)	0·6505 (1)	0·4721 (1)	0·0400 (3)
C(7B)	0·2624 (2)	0·3315 (1)	0·3796 (1)	0·0225 (3)
N(8B)	0·1943 (1)	0·2070 (1)	0·3886 (1)	0·0206 (2)
N(9B)	0·1104 (2)	0·2155 (1)	0·4951 (1)	0·0209 (2)
O(1)	0·4308 (2)	0·0885 (1)	0·2329 (1)	0·0313 (3)
O(2)	0·1205 (2)	0·1527 (1)	0·1141 (1)	0·0318 (3)
O(3)	0·2937 (2)	−0·0748 (1)	0·4341 (1)	0·0471 (4)
O(4)	0·5448 (2)	0·6838 (1)	0·2717 (1)	0·0424 (3)
H(1A)	0·360 (2)	−0·565 (2)	−0·149 (2)	0·038 (6)
H(2A)	0·217 (2)	−0·660 (2)	−0·020 (2)	0·035 (6)
H(7A)	0·360 (2)	−0·079 (2)	0·026 (2)	0·034 (5)
H(9A)	0·092 (2)	−0·275 (2)	0·231 (2)	0·034 (6)
H(11)	0·499 (3)	0·057 (2)	0·270 (2)	0·051 (8)
H(12)	0·463 (3)	0·153 (2)	0·213 (2)	0·049 (7)
H(21)	0·128 (3)	0·128 (2)	0·045 (2)	0·037 (6)
H(22)	0·028 (3)	0·150 (2)	0·121 (2)	0·050 (8)
H(31)	0·315 (3)	−0·026 (2)	0·510 (2)	0·061 (8)
H(32)	0·295 (3)	−0·148 (2)	0·438 (2)	0·046 (7)
H(41)	0·588 (3)	0·755 (2)	0·291 (2)	0·047 (7)
H(42)	0·496 (3)	0·661 (2)	0·323 (2)	0·043 (7)
H(1B)	0·194 (2)	0·690 (2)	0·665 (2)	0·044 (6)
H(2B)	0·047 (2)	0·565 (2)	0·765 (2)	0·030 (5)
H(7B)	0·312 (2)	0·344 (2)	0·311 (2)	0·035 (6)
H(9B)	0·068 (3)	0·133 (2)	0·519 (2)	0·064 (8)

Table 2. *Interatomic bond distances* (Å) *of* $Cu(allopurinol)_2SO_4.4H_2O$

Metal coordination polyhedra

Cu—N(8A)	2·002 (1)	Cu—O(2)	2·306 (1)
Cu—N(8B)	2·012 (1)	Cu—O(3)	2·290 (1)
Cu—O(1)	2·008 (1)	Cu—O(11)	2·033 (1)

Allopurinol

	Molecule A	Molecule B
N(1)—C(2)	1·359 (2)	1·356 (2)
C(2)—N(3)	1·304 (2)	1·306 (2)
N(3)—C(4)	1·364 (2)	1·367 (2)
C(4)—C(5)	1·390 (2)	1·391 (2)
C(5)—C(6)	1·432 (2)	1·434 (2)
C(6)—N(1)	1·383 (2)	1·390 (2)
C(5)—C(7)	1·402 (2)	1·404 (2)
C(7)—N(8)	1·323 (2)	1·323 (2)
N(8)—N(9)	1·362 (2)	1·368 (2)
N(9)—C(4)	1·343 (2)	1·342 (2)
C(6)—O(6)	1·234 (2)	1·227 (2)
N(1)—H(1)	0·83 (2)	0·86 (2)
C(2)—H(2)	0·91 (2)	0·94 (2)
C(7)—H(7)	0·92 (2)	0·88 (2)
N(9)—H(9)	0·83 (2)	0·93 (2)

S(1)—O(11)	1·507 (1)	S(1)—O(13)	1·480 (1)
S(1)—O(12)	1·474 (1)	S(1)—O(14)	1·452 (1)

Table 3. *Interatomic bond angles* (°) *of* $Cu(allopurinol)_2SO_4.4H_2O$

Metal coordination polyhedra

N(8A)—Cu—O(1)	86·9 (1)	O(1)—Cu—O(11)	175·7 (1)
N(8A)—Cu—O(2)	92·0 (1)	O(2)—Cu—N(8B)	87·7 (1)
N(8A)—Cu—N(8B)	177·5 (1)	O(2)—Cu—O(3)	176·5 (1)
N(8A)—Cu—O(3)	90·5 (1)	O(2)—Cu—O(11)	97·1 (1)
N(8A—Cu—O(11)	92·8 (1)	N(8B)—Cu—O(3)	89·7 (1)
O(1)—Cu—O(2)	87·2 (1)	N(8B)—Cu—O(11)	89·7 (1)
O(1)—Cu—N(8B)	90·7 (1)	O(3)—Cu—O(11)	85·3 (1)
O(1)—Cu—O(3)	90·4 (1)		

Allopurinol

	Molecule A	Molecule B
C(6)—N(1)—C(2)	124·7 (1)	124·5 (1)
N(1)—C(2)—N(3)	125·7 (1)	125·6 (1)
C(2)—N(3)—C(4)	111·8 (1)	112·3 (1)
N(3)—C(4)—C(5)	127·4 (1)	127·0 (1)
C(4)—C(5)—C(6)	118·6 (1)	118·6 (1)
C(5)—C(6)—N(1)	111·7 (1)	111·9 (1)
C(4)—C(5)—C(7)	105·1 (1)	105·1 (1)
C(5)—C(7)—N(8)	110·0 (1)	110·1 (1)
C(7)—N(8)—N(9)	107·1 (1)	107·0 (1)
N(8)—N(9)—C(4)	110·3 (1)	110·3 (1)
N(9)—C(4)—C(5)	107·5 (1)	107·5 (1)
N(3)—C(4)—N(9)	125·1 (1)	125·4 (1)
C(6)—C(5)—C(7)	136·3 (1)	136·3 (1)
N(1)—C(6)—O(6)	119·8 (1)	120·7 (1)
C(5)—C(6)—O(6)	128·5 (1)	127·4 (1)
C(2)—N(1)—H(1)	118 (1)	115 (1)
C(6)—N(1)—H(1)	117 (1)	121 (1)
N(1)—C(2)—H(2)	114 (1)	113 (1)
N(3)—C(2)—H(2)	120 (1)	122 (1)
C(5)—C(7)—H(7)	129 (1)	132 (1)
N(8)—C(7)—H(7)	121 (1)	117 (1)
C(4)—N(9)—H(9)	128 (1)	133 (2)
N(8)—N(9)—H(9)	122 (1)	116 (2)

Cu—N(8A)—C(7A)	128·3 (1)	Cu—N(8B)—N(9B)	123·7 (1)
Cu—N(8A)—N(9A)	124·0 (1)	Cu—O(11)—S(1)	122·7 (1)
Cu—N(8B)—C(7B)	129·3 (1)		
O(11)—S(1)—O(12)	108·6 (1)	O(12)—S(1)—O(13)	109·4 (1)
O(11)—S(1)—O(13)	107·1 (1)	O(12)—S(1)—O(14)	111·5 (1)
O(11)—S(1)—O(14)	109·8 (1)	O(13)—S(1)—O(14)	110·3 (1)

octahedral CuN_2O_4 coordination by two N(8)-coordinating allopurinol ligands arranged in *trans* positions and by four O atoms of three water molecules and one sulfate group. The apical positions of the (4 + 2)-distorted octahedron are occupied by two water O atoms. The noncoordinating water molecule is bonded to the monomeric complex unit by O—H···O hydrogen-bonding contacts. The (4 + 2)-distorted copper coordination octahedron is characterized by the following bond distances: Cu—N(8) = 2·002 (1) and 2·012 (1) Å, Cu—O_{SO_4} = 2·033 (1) Å, Cu—O_{H_2O} 2·008 (1) Å (equatorial plane); Cu—O_{H_2O} = 2·290 (1) and 2·306 (1) Å (apical positions). In contrast to the copper complex described here, the isostructural cobalt and cadmium analogues (Hänggi, Schmalle & Dubler, 1988*a*) exhibit only slightly distorted octahedra with bonding distances of the coordinating atoms ranging from 2·073 (1) to 2·151 (1) Å (Co) and from 2·267 (1) to 2·335 (1) Å (Cd). Interatomic bond distances and angles are listed in Tables 2 and 3, respectively.

Apart from the pronounced distortion of the copper coordination octahedron, the Cu complex is isostructural with its Co, Cd, Ni and Zn analogues (Hänggi, Schmalle & Dubler, 1988*a*). In these complexes neutral unsubstituted allopurinol is monodentately coordinating through N(8). In all complexes,

where coordination occurs through N(8), the H atoms are attached at N(1) and N(9) of the neutral allopurinol molecule. Metallation at the other pyrazole atom N(9) is only observed in the rhodium complex mentioned above, where the H atoms are covalently bonded to N(1) and N(8) (Sheldrick & Günther, 1988). In addition, N(9) is the metal binding site for the N(1), N(3) and N(8) protonated allopurinolium cation in the chlorine-bridged polymeric chain structure [CuCl₃(allopurinol⁺)]ₙ (Sheldrick & Bell, 1987a). The dianion of allopurinol is coordinating through N(9) and N(1) to different methylmercury cations, as established for [(CH₃Hg)₂(allopurinol²⁻)].2H₂O (Sheldrick & Bell, 1987b).

This series of systematic investigations on the coordination properties of allopurinol points to the fact that N(3) is the least basic site with respect to metal coordination. Crystal structure determinations show no evidence for any N(3) metallation of allopurinol. In contrast, in its 7-aza-8-deaza derivative hypoxanthine (hyxan), the atom N(3) was identified to be a competitive metal binding site. Bridging of two metal ions by N(3)/N(9)-chelating hypoxanthine molecules seems to be a common coordination type in dimeric structures of general formula [M₂(μ-hyxan)₂(SO₄)₂(μ-H₂O)₂(H₂O)₂] with M = Cu, Zn, Cd (Dubler, Hänggi & Schmalle, 1990) and of [Cu(μ-hyxan)₄Cl₂].2H₂O (Sletten, 1970). In Cu-(hyxan)SO₄.H₂O (Dubler, Hänggi & Bensch, 1987) coordination occurs through N(3) and N(7) to different metal ions, forming infinite copper hypoxanthine chains.

Taylor & Kennard (1982) have summarized the effects of protonation of N atoms on the geometry of different purine derivatives. For example, protonation induces an increase in the corresponding C—N—C angle in the imidazole ring of about 3–4°. We have shown that similar but much smaller alterations of the ring geometry are observed on metallation (Dubler, Hänggi & Schmalle, 1987; Dubler & Gyr, 1988). Bond distances and angles within the monodentate N(8)-coordinating allopurinol ligands of the copper complex described here, of the isostructural compounds M(allopurinol)₂SO₄.4H₂O (M = Co, Cd) (Hänggi, Schmalle & Dubler, 1988a) and of the cobalt chloro complex Co(allopurinol)₂-Cl₂.2H₂O (Hänggi, Schmalle & Dubler, 1988b) are in close agreement. The largest differences of corresponding bond lengths within seven crystallographically independent neutral allopurinol molecules is 0·016 Å observed for N(1)—C(2), and the largest difference of bond angles is 1·7° found for N(1)—C(6)—O(6). The bond angle C(7)—N(8)—N(9), reflecting the influence of metallation at N(8), is 107·1 (1) and 107·0 (1)° in Cu(allopurinol)₂SO₄.4H₂O. The respective angles for N(8)-

coordinating allopurinol found in the three other allopurinol complexes are in the range 106·5 (1)–107·1 (1)°. A comparison of the angle C(7)—N(8)—N(9) in neutral allopurinol (Prusinger & Sundaralingam, 1972) with the mean value determined from the seven N(8)-coordinated allopurinol ligands shows an alteration from 106·4 (1) to 106·9 (1)°. This increase is indicative of a very small but significant effect of metallation at N(8) on the ring geometry of neutral allopurinol.

The purine rings in the copper complex described here are approximately planar with a maximum deviation of 0·022 (2) Å for C(5A) and −0·025 (2) Å for C(4B) from the least-squares plane calculated through the nine ring atoms. The out-of-plane deviations for the extra-annular atoms O(6) are −0·031 (2) and −0·021 (2) Å, respectively.

The principal feature of the molecular packing in the unit cell is shown in Fig. 3. On the basis of the classification proposed by Bugg (1972), a solid-state stacking pattern of the purine rings of type II occurs, where the bases are stacked on top of each other rotated by about 180°. The infinitely stacked purine rings are nearly parallel with a dihedral angle between the purine planes of 8·0°. The mean stacking distance, calculated as the mean distance of individual atoms of a molecule from the least-squares plane through the stacking molecule, is 3·26 Å.

The layered structure of Cu(allopurinol)₂-SO₄.4H₂O exhibits an extended hydrogen-bonding system. Information concerning the geometry of hydrogen-bonding contacts is given in Table 4. The allopurinol ligands are involved in hydrogen bonds of the type N—H⋯N and N—H⋯O, whereas the coordinating water molecules participate in O—H⋯O hydrogen-bonding contacts. The atom O(4) of the noncoordinating water molecule is hydrogen bonded to O(6B) of an allopurinol ring and to O(13) of a sulfate group. In addition, a relatively strong N(1A)—H(1A)⋯O(4) hydrogen
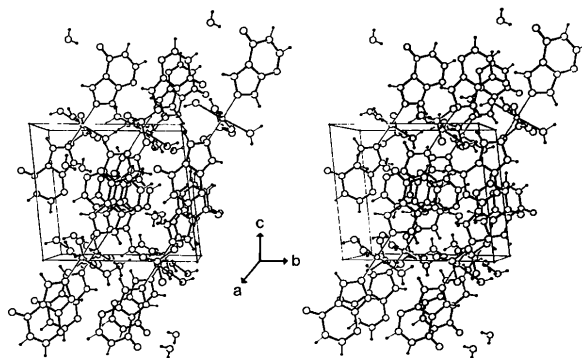

Fig. 3. *ORTEP* drawing of the packing diagram of Cu(allopurinol)₂SO₄.4H₂O.

Table 4. Hydrogen-bonding contacts in $Cu(allopurinol)_2SO_4.4H_2O$

$X—H···Y$	$X—H$ (Å)	$X···Y$ (Å)	$X—H···Y$ (°)
N(14)—H(14)···O(4)	0·83 (2)	2·726 (2)	169 (2)
N(9A)—H(9A)···N(3B)	0·83 (2)	2·858 (2)	155 (2)
N(1B)—H(1B)···O(12)	0·86 (2)	2·801 (2)	164 (2)
N(9B)—H(9B)···O(11)	0·93 (2)	2·908 (2)	142 (2)
O(1)—H(11)···O(13)	0·78 (2)	2·801 (2)	166 (2)
O(1)—H(12)···O(6A)	0·73 (2)	2·694 (2)	174 (3)
O(2)—H(21)···O(14)	0·77 (2)	2·738 (2)	167 (2)
O(2)—H(22)···O(12)	0·77 (2)	2·781 (2)	150 (2)
O(3)—H(31)···O(13)	0·91 (2)	2·745 (2)	165 (2)
O(3)—H(32)···O(6B)	0·73 (2)	2·837 (3)	168 (2)
O(4)—H(41)···O(13)	0·77 (2)	2·802 (2)	173 (2)
O(4)—H(42)···O(6B)	0·74 (2)	2·826 (2)	165 (2)

bond with a donor—acceptor distance of 2·726 (2) Å is observed between the allopurinol ligand and the noncoordinating water molecule.

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Structure of an Organometallic Polymer, [Na{(η⁵-C₅H₅)Co[P(O)(OMe)₂]₃}]ₙ

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Abstract. Sodium (η⁵-cyclopentadienyl)tris(dimethyl phosphito)cobaltate(1−), $M_r = 474·14$, orthorhombic, $Pna2_1$, $a = 18·195(8)$, $b = 9·436(3)$, $c = 11·316(5)$Å, $V = 1943$Å³, $Z = 4$, $D_x = 1·621$ g cm⁻³, $\lambda(MoK\alpha) = 0·71073$Å, $\mu = 11·83$ cm⁻¹, $F(000) = 976$, room temperature, final $R = 0·036$ for 1337 observed reflections with $I \geq 3\sigma(I)$. The title compound is polymeric. Each $[(C_5H_5)Co\{P(O)(OMe)_2\}_3]^-$ (L_{OMe}^-) fragment behaves as a bridging ligand between two Na atoms; one end of the bridge is constituted by three complexing P=O O atoms, the other by two O(Me) O atoms of two distinct $P(O)(OMe)_2$ groups. The coordination polyhedron around the Na ions is approximately square pyramidal.

Introduction. The coordination chemistry of ligands of the type $[(\eta^5\text{-}C_5H_5)Co\{P(O)(OR)_2\}_3]^-$ (L_R^-) has