Structure of [Co$_2$(μ-hypoxanthine)$_2$(SO$_4$)$_2$(μ-H$_2$O)$_2$(H$_2$O)$_2$]

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Abstract. Diaqua(1,7-dihydro-6*H*-purin-6-one)sulfatocobalt(II), [Co(C$_5$H$_4$N$_4$O)SO$_4$(H$_2$O)$_2$], M_r = 327.13, triclinic, $P\bar{1}$, a = 7.262 (2), b = 8.699 (1), c = 8.787 (3) Å, α = 102.68 (2), β = 91.62 (2), γ = 112.43 (2)°, V = 496.7 (5) Å^3, Z = 2, D_m = 2.19, D_x = 2.19 g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, μ = 18.69 cm^{-1}, $F(000)$ = 330, T = 295 K. The structure was solved on the basis of 5484 unique reflections and refined by full-matrix least-squares calculations to R = 0.034 using 4888 observed reflections with I > 3$\sigma(I)$. The Co complex has a dimeric structure. Two Co ions are bridged by two N(3)/N(9)-chelating hypoxanthine ligands and by two water molecules. The intramolecular Co—Co distance is 3.124 (1) Å. The coordinating hypoxanthine ligands are stacked with a minimum stacking distance of 3.29 Å, rotated about 180° with respect to each other. The dimeric structure is stabilized by strong O—H···O hydrogen bonds of the bridging water molecule with O···O distances of 2.607 (2) and 2.670 (2) Å, respectively.

Introduction. Hypoxanthine (1,7-dihydro-6*H*-purin-6-one) is a purine base which is not common in ribonucleic or deoxyribonucleic acids, but occurs occasionally as a constituent of the nucleoside inosine in minor amounts in transfer RNA (Hurst, 1980). Therefore hypoxanthine is a metabolic intermediate product of purine metabolism formed by degradation of inosine. The Mo- and Fe-containing enzyme xanthine oxidase is capable of catalyzing the oxidation of hypoxanthine *via* xanthine to uric acid. Defects in this metabolism result in an increase of the uric acid level, leading to deposits of sodium hydrogenurate monohydrate crystals in joints, which produce the painful symptoms of gout (Hille & Massey, 1985). In addition, crystalline hypoxanthine or xanthine may be deposited in muscle tissue as a consequence of the hereditary disease xanthinuria (Hesse & Bach, 1982).

Crystal structure determinations of metal complexes of neutral unsubstituted hypoxanthine have elucidated three different coordination types. In *monomeric* complexes hypoxanthine monodentately

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coordinates through the atom N(7) (Dubler, Hänggi & Bensch, 1987; Dubler, Hänggi & Schmalle, 1987; Kastner, Coffey, Clarke, Edmonds & Eriks, 1981). Two metal ions are bridged by four N(3)/N(9)-chelating hypoxanthine ligands in the *dimeric* complex [Cu$_2$(μ-hypoxanthine)$_4$Cl$_2$].3H$_2$O reported by Sletten (1970), whereas coordination through N(3) and N(7) to different metal ions is only observed in a *polymeric* Cu complex (Dubler, Hänggi & Bensch, 1987).

We recently reported on metal hypoxanthine complexes with the general formula M(hypoxanthine)-SO$_4$.2H$_2$O (M = Cu, Cd, Zn) which exhibit a new structure type: two metal ions are bridged by two N(3)/N(9)-chelating hypoxanthine ligands as well as by two water molecules (Dubler, Hänggi & Schmalle, 1990). The cell parameters of the corresponding Co complex Co(hypoxanthine)SO$_4$.2H$_2$O have now been established to be very similar to those of the complexes mentioned above and therefore indicate an isostructural relationship. To examine structural details of the molecular unit and of hydrogen-bonding contacts the structure analysis of the title compound has been carried out.

Experimental. To prepare single crystals of Co-(hypoxanthine)SO$_4$.2H$_2$O a solution of 700 mg (5.14 mmol) hypoxanthine and 10.0 g (42.03 mmol) CoCl$_2$.6H$_2$O in 10 ml 0.5 N H$_2$SO$_4$ was boiled under reflux for 12 h and then kept for crystallization at 348 K. Three months later, rose-coloured crystals of composition calculated as C 18.36, H 2.46, N 17.13, S 9.80, H$_2$O 11.01% and observed as C 18.69, H 2.60, N 16.85, S 10.07, H$_2$O 11.92% (thermogravimetric analysis) could be isolated.

Thermogravimetric data were recorded on a Perkin–Elmer TGS-2 thermobalance in flowing oxygen atmosphere. The thermal decomposition of Co(hypoxanthine)SO$_4$.2H$_2$O occurs in three rather poorly defined steps. In the first step the complex is dehydrated in the temperature range 503–313 K. The two structurally different types of water molecules are not distinguished within this first step, but the high dehydration temperature indicates that the water molecules are strongly linked by hydrogen

bonds. The observed weight loss on water elimination of 11.9% corresponds to the theoretical value for two water molecules per formula unit. The anhydrous Co complex is rapidly decomposed in two overlapping steps. The final residue is Co_3O_4 as evidenced by X-ray powder diffractometry and by the agreement of calculated and observed weight losses.

A single crystal with dimensions $0.57 \times 0.27 \times 0.20$ mm was selected for X-ray investigations. D_m was determined by flotation in a mixture of $CHCl_3$ and CH_2I_2. The lattice constants were obtained from least-squares refinement of the θ values of 25 reflections in the interval $13.5 < \theta < 18.5°$, collected on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation at 295 K. Intensities of 6182 reflections (including 124 standards) in the θ range of 1–40° were obtained using the ω–2θ scan technique with variable scan speeds between 1.8 and $8.2°$ min^{-1}. The scan width was set to $\Delta\omega =$ $(0.90 + 0.35\tan\theta)°$. The index range was $-13 \le h \le$ 13, $-15 \le k \le 15$, $0 \le l \le 15$. Four standard reflections monitored every 3 h of measuring time showed no significant decrease of intensities. Orientation was controlled every 300 reflections using four standard reflections. 325 reflections had negative intensities and were excluded from the data set. Data reduction (498 reflections averaged, $R_{int} = 0.019$) led to 5484 unique reflections. The data were corrected for Lorentz and polarization effects, and a numerical absorption correction based on ten indexed crystal faces was applied (minimum and maximum transmission factors 0.57 and 0.80, respectively).

The structure was solved by Patterson syntheses and difference Fourier methods. The refinement was started with the atomic coordinates of the non-H atoms of the isostructural Cd complex (Dubler, Hänggi & Schmalle, 1990). Full-matrix least-squares refinement cycles (on F) were carried out with SHELX76 (Sheldrick, 1976) by minimizing $\Sigma w(||F_o|$ $- |F_c||)^2$ with $w = K/\sigma^2(F_o)$ ($K = 0.665$) using 4888 reflections with $I \ge 3\sigma(I)$, $\sigma(I)$ based on counting statistics using the CAD-4 measurements procedure of the Enraf–Nonius (1984) Operator's Guide. All H atoms could be localized in the difference Fourier maps, but were not refined. The isotropic thermal parameters U of all H atoms were fixed at 0.04 Å^2. Final refinement with 4888 observed reflections and 163 parameters converged to $R = 0.034$ and $wR =$ 0.036. The maximum final shift to e.s.d. ratio was 0.01. Maximum and minimum electron densities in final difference Fourier synthesis were 1.17 e Å^{-3}, located 0.88 Å from O(6), and -0.72 e Å^{-3}, located at a distance of 1.15 Å from C(6). Atomic scattering factors for the neutral atoms and anomalous-dispersion terms for C, H, N, O, S were those of SHELX76, for Co they were taken from Interna

tional Tables for X-ray Crystallography (1974, Vol IV). All calculations were performed on an NAS AS/XL V60 and a PDP 11/34 computer. The refined atomic and isotropic thermal parameters are listed in Table 1.*

Discussion. The dimeric Co complex, shown in Fig. 1, consists of molecular centrosymmetric units of the type [$Co_2(\mu$-hypoxanthine)$_2(SO_4)_2(\mu$-$H_2O)_2(H_2O)_2$]. Two Co ions are bridged by two N(3)/N(9)-chelating hypoxanthine ligands and by two water molecules. The intramolecular Co—Co distance between the symmetry related octahedral units is 3.124 (1) Å. The coordination polyhedron of each Co ion is completed by another water molecule and a sulfate group. Interatomic bond distances and angles with their standard deviations are listed in Table 2. The bond lengths are in the usually observed ranges, and the Co—O distances of the bridging water molecules are significantly longer than those of the terminal water molecules. The CoN_2O_4 coordination polyhedron is markedly distorted, evidenced by the octahedra-defining angles which vary between 81.9 (1) and 98.5 (1)°. The Co ion is displaced by 0.042 Å in a direction toward the atom N(9) from the weighted best plane defined by the four coordinating O atoms. The angle of 88.7° between the

Table 1. *Positional and thermal parameters* (Å^2) *of* Co(*hypoxanthine*)SO$_4$.2H$_2$O

Equivalent isotropic thermal parameters for non-H atoms:
$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*.\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}/U_{iso}
Co	0.02082 (3)	0.19000 (2)	0.05351 (2)	0.01423 (3)
S(1)	−0.31349 (5)	0.31304 (4)	0.22233 (4)	0.01444 (4)
O(11)	−0.3754 (2)	0.4491 (1)	0.1916 (1)	0.0212 (2)
O(12)	−0.4688 (2)	0.1430 (1)	0.1554 (2)	0.0269 (2)
O(13)	−0.2701 (3)	0.3453 (2)	0.3922 (2)	0.0426 (4)
O(14)	−0.1277 (2)	0.3345 (2)	0.1498 (2)	0.0376 (4)
N(1)	0.2687 (2)	0.2827 (2)	0.5368 (2)	0.0217 (2)
C(2)	0.1935 (3)	0.2883 (2)	0.3986 (2)	0.0221 (3)
N(3)	0.1293 (2)	0.1608 (2)	0.2728 (1)	0.0181 (2)
C(4)	0.1479 (2)	0.0150 (2)	0.2957 (2)	0.0165 (2)
C(5)	0.2229 (2)	0.0007 (2)	0.4354 (2)	0.0195 (2)
C(6)	0.2904 (2)	0.1396 (2)	0.5708 (2)	0.0212 (3)
O(6)	0.3591 (2)	0.1433 (2)	0.7020 (1)	0.0323 (3)
N(7)	0.2150 (2)	−0.1629 (2)	0.4108 (2)	0.0213 (2)
C(8)	0.1377 (3)	−0.2400 (2)	0.2595 (2)	0.0215 (3)
N(9)	0.0934 (2)	−0.1381 (2)	0.1857 (2)	0.0181 (2)
O(1)	0.2111 (2)	0.0567 (1)	−0.0401 (1)	0.0161 (2)
O(2)	0.2604 (2)	0.4220 (2)	0.0692 (2)	0.0229 (2)
H(1)	0.306	0.365	0.610	0.040
H(2)	0.184	0.370	0.385	0.040
H(7)	0.259	−0.198	0.471	0.040
H(8)	0.104	−0.357	0.212	0.040
H(11)	0.248	0.075	−0.125	0.040
H(12)	0.319	0.079	0.019	0.040
H(21)	0.375	0.437	0.108	0.040
H(22)	0.270	0.454	−0.007	0.040

plane through the four binding N atoms and the plane defined by M—O(1)—M—O(2) also indicates a small deviation from the ideal octahedral geometry.

The dimeric structure of the Co complex described here is quite similar to the structure of the copper complex [Cu$_2$(μ-hypoxanthine)$_4$Cl$_2$].3H$_2$O (Sletten, 1970). The main difference is that in the latter complex two Cu ions are bridged by four N(3)/N(9)-chelating hypoxanthine ligands, whereas in the title compound two Co ions are bridged by only two hypoxanthine ligands and by two water molecules.

The crystal structure analysis of neutral hypoxanthine revealed that the H atoms are predominantly attached at N(1) and N(9) in the solid state (Schmalle, Hänggi & Dubler, 1988). This tautomer has also been found in all monomeric and polymeric metal complexes containing neutral unsubstituted hypoxanthine. In contrast, in the dimeric complexes described here, where N(3) and N(9) of the bidentate hypoxanthine ligand are involved in coordination to the metals, the H atoms are bonded to the remaining N atoms N(1) and N(7).

An interesting structural feature of this dimeric complex is the unusual bridging bonding mode of the two water molecules. Whereas OH$^-$ or O^{2-} are quite well known as bridging ligands only a few structures have been reported where two Co atoms are bridged by an O atom of a water molecule. These dinuclear Co complexes may be represented by the general formula [Co$_2$(μ-H$_2$O)(μ-O$_2$CR)$_2$(O$_2$CR)(tmen)$_2$], where tmen = N,N,N',N'-tetramethylethylenediamine and R = CH$_3$, CH$_2$Cl, CHCl$_2$ or CCl$_3$. The bonding
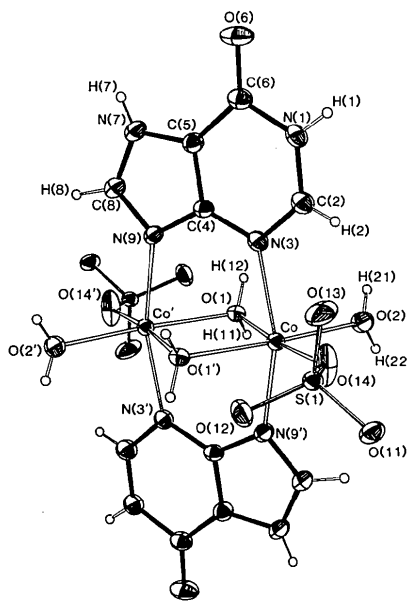
Table 2. *Interatomic bond distances* (Å) *and angles* (°) *in* Co(*hypoxanthine*)SO$_4$.2H$_2$O

Co—N(3)	2.163 (1)	Co—O(1')	2.139 (1)
Co—N(9')	2.124 (1)	Co—O(2)	2.075 (1)
Co—O(1)	2.191 (1)	Co—O(14)	2.019 (1)
Co—Co'	3.124 (1)	C(5)—N(7)	1.370 (2)
N(1)—C(2)	1.335 (2)	N(7)—C(8)	1.346 (2)
C(2)—N(3)	1.307 (2)	C(8)—N(9)	1.329 (2)
N(3)—C(4)	1.382 (2)	N(9)—C(4)	1.369 (2)
C(4)—C(5)	1.379 (2)	C(6)—O(6)	1.232 (2)
C(5)—C(6)	1.414 (2)	N(3)—N(9)	2.452 (2)
C(6)—N(1)	1.405 (2)	S(1)—O(13)	1.459 (1)
S(1)—O(11)	1.489 (1)	S(1)—O(14)	1.472 (1)
S(1)—O(12)	1.455 (1)		

N(3)—Co—N(9')	162.0 (1)	N(9')—Co—O(14)	98.3 (1)
N(3)—Co—O(1)	81.9 (1)	O(1)—Co—O(1')	87.7 (1)
N(3)—Co—O(1')	84.2 (1)	O(1)—Co—O(2)	88.9 (1)
N(3)—Co—O(2)	93.3 (1)	O(1)—Co—O(14)	174.0 (1)
N(3)—Co—O(14)	96.1 (1)	O(1')—Co—O(2)	176.0 (1)
N(9')—Co—O(1)	84.8 (1)	O(2)—Co—O(14)	85.6 (1)
N(9')—Co—O(1')	83.2 (1)	O(1')—Co—O(14)	97.8 (1)
N(9')—Co—O(2)	98.5 (1)	C(5)—N(7)—C(8)	105.8 (1)
C(6)—N(1)—C(2)	125.8 (1)	N(7)—C(8)—N(9)	112.9 (1)
N(1)—C(2)—N(3)	125.1 (2)	C(8)—N(9)—C(4)	105.1 (1)
C(2)—N(3)—C(4)	112.9 (1)	N(9)—C(4)—C(5)	109.1 (1)
N(3)—C(4)—C(5)	124.8 (1)	N(3)—C(4)—N(9)	126.1 (1)
C(4)—C(5)—C(6)	121.6 (2)	C(6)—C(5)—N(7)	131.3 (2)
C(5)—C(6)—N(1)	109.8 (1)	N(1)—C(6)—O(6)	122.2 (1)
C(4)—C(5)—N(7)	107.1 (1)	C(5)—C(6)—O(6)	128.0 (2)
Co—N(3)—C(2)	121.3 (1)	Co—N(9')—C(8')	128.7 (1)
Co—N(3)—C(4)	125.8 (1)	Co—O(14)—S(1)	138.9 (1)
Co—N(9')—C(4')	126.1 (1)	O(12)—S(1)—O(13)	111.4 (1)
O(11)—S(1)—O(12)	111.0 (1)	O(12)—S(1)—O(14)	110.9 (1)
O(11)—S(1)—O(13)	107.5 (1)	O(13)—S(1)—O(14)	109.5 (1)
O(11)—S(1)—O(14)	106.3 (1)		

characteristics of such dimeric water-bridged complexes are summarized in Table 3. In all of these complexes the bridging water molecules are involved in two short hydrogen-bonded contacts of the type O—H···O.

The molecular dimensions of the hypoxanthine ligand in the structure presented here are in close agreement with the values obtained for M(hypoxanthine)SO$_4$.2H$_2$O with M = Cu, Cd (Dubler, Hänggi & Schmalle, 1990). Taylor & Kennard (1982) have demonstrated that H atom attachment at a ring N atom of purine derivatives induces a widening of the corresponding C—N—C angle by about 4° and a decrease of the adjacent angles by about 2–3°, a fact also observed for the oxopurine hypoxanthine (Schmalle, Hänggi & Dubler, 1988). In addition, it has been shown that metal coordination at an N atom in oxopurines induces changes in the geometry of the purine moiety similar to, but much smaller than, those induced by protonation at the respective N atom (Dubler, Hänggi & Schmalle, 1987; Dubler, Hänggi & Bensch, 1987). Comparing the bond angles, listed in Table 2, with the mean values of the two independent hypoxanthine molecules in neutral uncomplexed hypoxanthine, structural changes typical for N(3)/N(9) chelation are observed. The bond angle C(2)—N(3)—C(4), 112.1 (1)° in hypoxanthine, where no H atom is attached at N(3), is enlarged to 112.9 (1)° upon N(3) coordination. In contrast the angle C(4)—N(9)—C(8) is decreased from 106.8 (1)° in hypoxanthine, where an H atom is bonded to

Fig. 1. *ORTEP* (Johnson, 1965) drawing of the dimeric unit [Co$_2$(μ-hypoxanthine)$_2$(SO$_4$)$_2$(μ-H$_2$O)$_2$(H$_2$O)$_2$].

Table 3. *Bonding characteristics* (Å, °) *of bridging water molecules in dimeric* Co *complexes*

Dimeric unit*	M—M'	O—M	O—M'	M—O—M'	O(H1)···O	O(H2)···O	O—H(1)—O	O—H(2)—O	References
[Co₂(μ-hyxan)₂(SO₄)₂(μ-H₂O)₂(H₂O)₂]	3.124 (1)	2.191 (1)	2.139 (1)	92.4 (1)	2.670 (2)	2.607 (2)	172	173	This work
[Co₂(μ-H₂O)(μ-ac⁻)₂(ac⁻)₂(tmen)₂]	3.597 (1)	2.147 (3)	2.117 (3)	115.1 (1)	2.565 (4)	2.548 (4)	160†	173†	Turpeinen, Ahlgrén & Hämäläinen (1982)
[Co₂(μ-H₂O)(μ-Cl-ac⁻)₂(Cl-ac⁻)₂(tmen)₂]	3.621 (1)	2.165 (2)	2.165 (2)	113.5 (2)	2.597 (3)	2.597 (3)	158†	158†	Turpeinen, Ahlgrén & Hämäläinen (1982)
[Co₂(μ-H₂O)(μ-Cl₂-ac⁻)₂(Cl₂-ac⁻)₂(tmen)₂]	3.675 (1)	2.156 (3)	2.169 (3)	116.4 (1)	2.567 (5)	2.608 (5)	‡	‡	Ahlgrén, Hämäläinen & Turpeinen (1983)
[Co₂(μ-H₂O)(μ-Cl₃-ac⁻)₂(Cl₃-ac⁻)₂(tmen)₂]	3.696 (3)	2.18 (1)	2.18 (1)	116.1 (6)	2.56 (2)	2.60 (2)	‡	‡	Turpeinen, Hämäläinen & Reedijk (1987)

* Abbreviation of ligand names; hyxan, hypoxanthine; tmen, *N,N,N',N'*-tetramethylethylenediamine; ac⁻, acetato; Cl-ac⁻, chloroacetato; Cl₂-ac⁻, dichloroacetato; Cl₃-ac⁻, trichloroacetato.

† Values not given in the original reference paper, but calculated on the basis of published atomic coordinates.

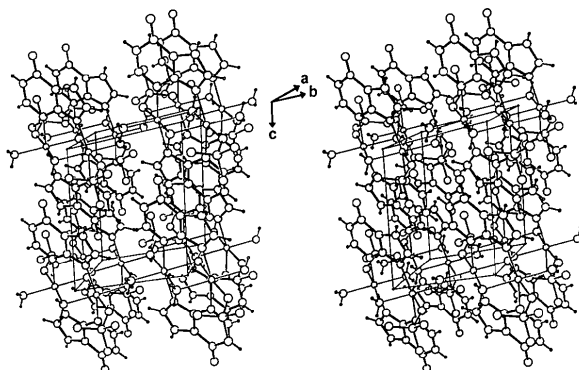‡ H-atom positions and/or hydrogen-bonding contacts not established.

Fig. 2. *ORTEP* (Johnson, 1965) drawing of the packing diagram in Co(hypoxanthine)SO₄.2H₂O.

Table 4. *Hydrogen-bonding geometry* (Å, °) *in* Co(*hypoxanthine*)SO₄.2H₂O

X—H···Y	X—H	H···Y	X···Y	X—H···Y
N(1)—H(1)···O(11)	0.80	2.00	2.795 (2)	172
N(1)—H(1)···O(13)	0.80	2.63	3.155 (2)	125
N(7)—H(7)···O(13)	0.78	1.96	2.700 (3)	160
O(1)—H(11)···O(6)	0.83	1.85	2.670 (2)	172
O(1)—H(12)···O(12)	0.86	1.75	2.607 (2)	173
O(2)—H(21)···O(11)	0.84	1.89	2.732 (2)	175
O(2)—H(22)···O(11)	0.77	2.03	2.781 (2)	164

Hydrogen-bond distances and angles are listed in Table 4. The atom H(1) of the hypoxanthine ligand participates in a bifurcated hydrogen bond to O(11) and O(13) of the sulfate group. An additional N—H···O hydrogen bond to O(13) is found around H(7). The terminal water molecule is hydrogen bonded to O(11) with O···O distances of 2.732 (2) and 2.781 (2) Å, respectively. Strong hydrogen-bonding contacts with donor–acceptor distances of 2.670 (2) and 2.607 (2) Å are observed between the bridging water molecule and the exocyclic atom O(6) of the hypoxanthine ring and the atom O(12) of the sulfate anion, respectively.

N(9), to 105.1 (1)° upon N(9) coordination. The largest differences in the ring geometry are observed for the adjacent angles to the coordination sites. The angle N(3)—C(4)—C(5) is changed to 124.8 (1)° with respect to the mean value of 127.5 (2)° in hypoxanthine, whereas the angle N(9)—C(4)—C(5) is widened from 105.6 (2) (hypoxanthine) to 109.1 (1)°. In addition the 'bite' distance N(3)···N(9) of 2.430 (2) and 2.429 (2) Å in hypoxanthine is increased to 2.452 (2) Å in the Co complex.

The purine ring in the Co complex described here is perfectly planar with a maximum deviation of 0.006 Å of the atom N(1) from the least-squares plane calculated through the nine ring atoms. The extra-annular O atom O(6) lies 0.014 Å below this purine plane.

From the stereodrawing in Fig. 2 it is evident that a stacking pattern of type II occurs (Bugg, 1972). The stacking bases are rotated approximately 180° with respect to each other. The infinitely stacked hypoxanthine molecules, related by a centre of inversion, show only minor direct overlap because the rings are not perpendicular in relation to their translation axis. The shortest stacking distance between the coordinating hypoxanthine ligands, calculated as the mean distance of all ring atoms of a molecule from the least-squares plane through the stacking molecules, is 3.288 Å.

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Structures of Dichloro[(S)-methionine-N,S]platinum(II) and Chloro[glycyl-(S)-methioninato-N,N',S]platinum(II) Monohydrate

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Abstract. (I) [Pt{CH$_3$SCH$_2$CH$_2$CH(NH$_2$)COOH}Cl$_2$], M_r = 415.20, monoclinic, $P2_1$, a = 7.578 (2), b = 10.213 (2), c = 13.563 (4) Å, β = 98.77 (1)°, V = 1037.4 (4) Å^3, D_x = 2.657 g cm^{-3} for Z = 4, λ(Mo $K\alpha$) = 0.71069 Å, μ = 142.81 cm^{-1}, $F(000)$ = 768, T = 294 K, final R = 0.029 for 2980 reflections. (II) [Pt{H$_2$NCH$_2$CONCH(CO$_2$H)CH$_2$CH$_2$SCH$_3$}Cl].H$_2$O, M_r = 453.81, orthorhombic, $P2_12_12_1$, a = 6.9971 (4), b = 10.6246 (9), c = 16.965 (1) Å, V = 1261.2 (2) Å^3, D_x = 2.389 g cm^{-3} for Z = 4, λ(Mo $K\alpha$) = 0.71069 Å, μ = 115.69 cm^{-1}, $F(000)$ = 856, T = 294 K, final R = 0.021 for 1820 reflections. The structures of the title complexes have been redetermined using high-resolution data. In the asymmetric unit of (I) there are two independent diastereomeric molecules, the S atoms having opposite chiralities. The amino acid coordinates *via* the N(amino) and S(thioether) atoms, Pt—N(amino) 2.047 (8), 2.029 (8), Pt—S 2.246 (2), 2.247 (2) Å. In (II) the dipeptide coordinates *via* the N(amino), N(peptide) and S(thioether) atoms, Pt—N(amino) 2.046 (5), Pt—N(peptide) 2.004 (4), Pt—S 2.258 (2) Å.

Introduction. The use of Pt complexes in cancer chemotherapy (Rosenberg, Van Camp & Krigas, 1965; Rosenberg, Van Camp, Trosko & Mansour, 1969; Pinto & Lippard, 1985), and the role of Pt–protein and Pt–peptide interactions in processes which cause the wastage and toxic side effects of such drugs (Berners-Price & Kuchel, 1990; Lempers & Reedijk, 1990) have provided a new focus for interest in the structures of Pt–amino acid and Pt–peptide complexes. For example, the structures of

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the platinum(II) complexes of ethylcysteine (Theodorou, Photaki, Hadjiliadis, Gellert & Bau, 1982), ethionine (Khan, Venkatasubramanian, Najmuddin, Shamsuddin & Zakeeruddin, 1991) and thioglycine (Zahn, Polborn & Beck, 1989) have been reported recently. The structures of dichloro-(S)-methionineplatinum(II), (I), and of chloroglycl-(S)-methioninatoplatinum(II) monohydrate, (II), were reported in a preliminary publication by Freeman & Golomb (1970). We have redetermined these structures using high-resolution data.
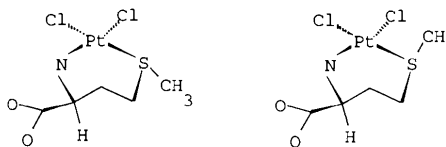
(I) molecule 1: *R* chirality at sulfur.   (I) molecule 2: *S* chirality at sulfur.

Experimental. Heating equimolar H$_2$O solutions of K$_2$PtCl$_4$ and (S)-methionine for (I) and glycyl-(S)-methionine for (II) gave yellow solids, which when recrystallized from H$_2$O and dilute HCl yielded good yellow prismatic crystals.

Crystals were mounted on glass fibres with epoxy resin. Data were collected on an Enraf–Nonius CAD-4 automatic diffractometer using graphite-monochromated Mo $K\alpha$ radiation. 25 independent reflections with $20 \le 2\theta \le 30°$ were used for least-squares determination of cell constants. Intensities of three reflections were monitored, and indicated less than 2.5% decomposition for (I) and less than 1.0% for (II). Both structures were solved by heavy-atom methods and refined (on F) by full-matrix least squares with an empirical correction for extinction.