

(C_s) symmetry, and the two independent molecules are essentially identical. In fact, a least-squares fit (Rohrer & Smith, 1980) of the relative positions of equivalent atoms in the two molecules yields an average separation of 0.09 (5) Å, with maximum separation 0.23 Å at C(3)···C(3'). Thus, although some small, statistically significant differences in 'chemically equivalent' geometric measures can be found,* only weighted averages are reported herein (Table 2).

The four pyridine rings are planar (r.m.s. deviation 0.01 Å)* with dihedral angles 48 and 55° (molecules 1 and 2 respectively). Each P atom is out-of-plane by *ca* 0.1 Å, and the two Co atoms are within 0.08 Å of three of the pyridine planes. Co(1) is 0.2 Å from the plane containing N(1), a distortion due perhaps to intermolecular forces in the disordered structure. Each phenyl ring is planar (r.m.s. deviation 0.004 Å) and locked into an orientation parallel to the mean molecular plane through very close contact with pyridine H atoms: H···C = 2.75 Å (calculated 2.9 Å; Pauling, 1960). Torsion angles have been deposited.

Most of the bond lengths and angles are similar to those previously reported. However, the N—Co—N angle varies considerably and seems to depend largely on the stereochemical requirements of the substituted pyridine ring. Thus, in the unrestricted 4-substituted complexes (Admiraal & Gafner, 1968; Laing & Carr, 1975) the N—Co—N angle is near the tetrahedral value. With a bulkier 2-substituent (Allan, Jones & Sawyer, 1981), this angle is slightly expanded to 114°, while in the seven-membered chelate ring (Kadooka, Warner & Seff, 1976) the angle is greatly expanded to 118°. In the current six-membered chelate ring, the angle is reduced to 95°.

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* See deposition footnote.

Table 2. Average geometry

Co—Cl	2.221 (1) Å	Cl—Co—Cl	116.2 (1)°
Co—N	2.031 (2)	Cl(1)—Co—N	108.7 (1)
P—C(Ph)	1.816 (4)	Cl(2)—Co—N	113.2 (1)
P—C(ph)	1.843 (3)	N—Co—N	94.8 (1)
N—C	1.347 (2)	C—P—C	102.3 (1)
C—C(py)	1.371 (2)	C—N—C	118.5 (3)
C—C(Ph)	1.379 (2)	C(1)—N—Co	119.4 (2)
		C(5)—N—Co	122.0 (2)
		N—C(1)—C(2)	123.1 (3)
		N—C(5)—C(4)	120.7 (3)
		P—C—N	116.6 (2)
		P—C—C(py)	122.2 (2)
		P—C(11)—C(12)	116.6 (3)
		P—C(11)—C(16)	124.7 (3)
		C—C—C(py)	119.2 (2)
		C—C—C(Ph)	119.9 (2)

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Monopotassium Salt of 4-Methyl[1,2,5]thiadiazolo[3,4-c][1,2,6]thiadiazine-7(6H)-one 5,5-Dioxide, C₄H₃N₄O₃S₂·K⁺

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Abstract. $M_r = 258.33$, monoclinic, $C2/c$, $a = 0.026$ for 1714 observed reflexions. The thiadiazine ring shows the expected envelope conformation. The K⁺ ion is mainly surrounded by seven neighbours at distances ranging from 2.72 (4) to 3.10 (1) Å forming a laterally capped trigonal prism.

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Introduction. The title compound has been prepared by Dr C. Ochoa (Instituto Química Médica, CSIC, Madrid) as part of a research programme on heterocyclic compounds containing the thiadiazine ring, aimed at investigating substances with potential biological activity (García-Muñoz, Ochoa, Stud & Pfeleiderer, 1976). The crystal structures of other related heterocycles have been reported recently (Esteban-Calderón, Martínez-Ripoll & García-Blanco, 1982c). The capability of these compounds to form alkaline salts has also been reported (Cabezuelo, Cano, Foces-Foces & García-Blanco, 1977; Esteban-Calderón, Martínez-Ripoll & García-Blanco, 1982a,b).

Experimental. Pale-yellow single crystal: $0.04 \times 0.05 \times 0.05$ cm. Four-circle CAD-4 diffractometer, $\theta \leq 30^\circ$, $\omega/2\theta$ scan technique. Unit cell: 21 reflexions, $4 < \theta < 30^\circ$, least-squares refinement. No absorption correction. Two standard reflexions: no intensity decay. 2737 unique reflexions, 1714 considered observed [$I > 4\sigma(I)$]. MULTAN80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) not successful for structure solution. Partial interpretation of Patterson map and subsequent use of DIRDIF (Beurskens, Bosman, Doesburg, Gould, Van den Hark & Prick, 1980) revealed the whole structure. Remaining calculations with XRAY70 (Stewart, Kundell & Baldwin, 1970). H atoms located at their calculated positions (Fayos & Martínez-Ripoll, 1975). Refinement (non-H atoms anisotropic) by full matrix least squares minimizing $\sum w|\Delta F|^2$ with $w = 1$ until convergence obtained. Last steps of refinement carried out with appropriate weighting scheme to give flat dependence on $\langle w|\Delta F|^2 \rangle$ vs $\langle F_o \rangle$ and vs $\langle \sin\theta/\lambda \rangle$ (Martínez-Ripoll & Cano, 1975). Scattering factors for neutral atoms and anomalous-dispersion corrections for S and K from *International Tables for X-ray Crystallography* (1974). Final $R = 0.026$, $wR = 0.022$, $S = 0.12$. $(\Delta/\sigma)_{\max} = 0.0009$. Difference map excursions $< 0.2 e \text{ \AA}^{-3}$. No correction for secondary extinction.

Discussion. Table 1 contains a list of atomic parameters.* Fig. 1 shows a partial view of the structure with the nearest neighbouring atoms and their labels. The best molecular plane is that defined by the five-membered ring, the maximum atomic deviation being 0.005 (7) Å. The thiadiazine ring has an envelope conformation with the S atom at the flap, 0.171 (4) Å out of the plane, as commonly occurs in similar compounds (Esteban-Calderón, Martínez-Ripoll & García-Blanco, 1982c). The distribution of bond lengths

and angles within the molecule (Table 2) indicates an electronic distribution with double bonds at C(2)=N(3) and C(3)=N(4). The significant difference between the two S(1)—N distances could be due to some degree of polarization, leaving the S atom with an electronic deficiency, which can be neutralized by a further electronic delocalization as shown in Fig. 2.

Table 1. Atomic parameters

$$U_{eq} = \frac{1}{3} \sum U_{ij} a_i^* a_j^* a_i a_j \cos(a_i a_j) \times 10^4.$$

	x	y	z	$U_{eq}(\text{Å}^2)$
K	0.70851 (2)	0.34362 (5)	0.79907 (6)	316 (3)
S(1)	0.66447 (2)	0.70515 (5)	0.81515 (6)	251 (3)
S(2)	0.55561 (2)	1.12616 (5)	0.61505 (8)	332 (3)
O(1)	0.69404 (6)	0.65004 (19)	0.68206 (21)	407 (6)
O(2)	0.65298 (7)	0.59840 (18)	0.94262 (22)	467 (7)
O(3)	0.70682 (6)	1.07241 (16)	0.96699 (21)	364 (6)
C(1)	0.67943 (7)	0.97613 (20)	0.88991 (24)	239 (6)
C(2)	0.62986 (7)	1.00896 (20)	0.77250 (24)	230 (6)
C(3)	0.59551 (7)	0.90138 (20)	0.69028 (24)	227 (5)
C(4)	0.57187 (10)	0.65137 (27)	0.61207 (38)	485 (9)
N(1)	0.69200 (7)	0.83726 (19)	0.91658 (24)	337 (6)
N(2)	0.60710 (7)	0.75769 (18)	0.70377 (25)	334 (7)
N(3)	0.61274 (7)	1.13935 (17)	0.74093 (22)	289 (6)
N(4)	0.55243 (6)	0.94899 (19)	0.59766 (23)	316 (6)

Table 2. Bond lengths (Å) and angles (°) with e.s.d.'s in parentheses

S(1)—O(1)	1.43 (2)	S(1)—O(2)	1.43 (1)
S(1)—N(1)	1.56 (1)	S(1)—N(2)	1.67 (2)
S(2)—N(3)	1.64 (3)	S(2)—N(4)	1.66 (1)
N(1)—C(1)	1.35 (1)	N(2)—C(3)	1.38 (1)
N(2)—C(4)	1.45 (1)	N(3)—C(2)	1.31 (1)
N(4)—C(3)	1.31 (2)	C(1)—C(2)	1.48 (2)
C(1)—O(3)	1.23 (1)	C(2)—C(3)	1.42 (1)
C(4)—H(41)	1.00	C(4)—H(42)	1.01
K—O(3)	2.72 (4)	K—O(3)	2.83 (1)
K—O(2)	2.88 (4)	K—O(1)	2.92 (1)
K—O(1)	3.00 (1)	K—O(2)	3.05 (2)
K—O(1)	3.10 (1)		
O(1)—S(1)—O(2)	112.8 (1)	O(1)—S(1)—N(1)	111.2 (1)
O(1)—S(1)—N(2)	107.2 (1)	O(2)—S(1)—N(1)	110.9 (1)
O(2)—S(1)—N(2)	105.9 (1)	N(1)—S(1)—N(2)	108.7 (1)
N(3)—S(2)—N(4)	98.6 (1)	S(1)—N(1)—C(1)	127.3 (1)
S(1)—N(2)—C(3)	119.5 (1)	S(1)—N(2)—C(4)	119.3 (2)
C(3)—N(2)—C(4)	121.1 (2)	S(2)—N(3)—C(2)	106.8 (1)
S(2)—N(4)—C(3)	105.6 (1)	N(1)—C(1)—C(2)	117.3 (2)
N(1)—C(1)—O(3)	121.5 (2)	C(2)—C(1)—O(3)	121.1 (2)
C(1)—C(2)—C(3)	123.1 (2)	C(1)—C(2)—N(3)	123.0 (2)
C(3)—C(2)—N(3)	113.9 (2)	N(2)—C(3)—C(2)	122.7 (2)
N(2)—C(3)—N(4)	122.2 (2)	N(4)—C(3)—C(2)	115.1 (2)
H(41)—C(4)—N(2)	120	H(42)—C(4)—N(2)	108
H(43)—C(4)—N(2)	108	H(41)—C(4)—H(42)	106
H(41)—C(4)—H(43)	107	H(42)—C(4)—H(43)	108
O(1)—K—O(3 ⁱⁱⁱ)	166.9 (1)	O(1)—K—O(3 ⁱ)	88.0 (1)
O(1)—K—O(1 ^{iv})	129.6 (1)	O(1)—K—O(1 ^{iv})	103.5 (1)
O(1)—K—O(2 ^v)	61.9 (1)	O(2)—K—O(3 ⁱⁱⁱ)	120.5 (1)
O(2)—K—O(3 ⁱ)	86.2 (1)	O(2)—K—O(1 ^{iv})	149.7 (1)
O(2)—K—O(1 ^{iv})	60.8 (1)	O(2)—K—O(2 ^v)	88.5 (1)
O(3 ⁱⁱⁱ)—K—O(3 ⁱ)	92.3 (1)	O(3 ⁱⁱⁱ)—K—O(1 ^{iv})	61.4 (1)
O(3 ⁱⁱⁱ)—K—O(1 ^{iv})	65.0 (1)	O(3 ⁱⁱⁱ)—K—O(2 ^v)	122.4 (1)
O(3 ⁱ)—K—O(1 ^{iv})	63.7 (1)	O(3 ⁱ)—K—O(1 ^{iv})	65.1 (1)
O(3 ⁱ)—K—O(2 ^v)	141.9 (1)	O(1 ^{iv})—K—O(1 ^{iv})	100.8 (1)
O(1 ^{iv})—K—O(2 ^v)	116.8 (1)	O(1 ^{iv})—K—O(2 ^v)	140.6 (1)
O(1)—K—O(2)	46.5 (1)		

Symmetry code

(i) $1.5 - x, 1.5 - y, 2 - z$ (ii) $x, -1 + y, z$ (iii) $x, 1 - y, -0.5 + z$ (ii) $1.5 - x, -0.5 + y, 1.5 - z$ (iv) $x, 1 - y, 0.5 + z$

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38897 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

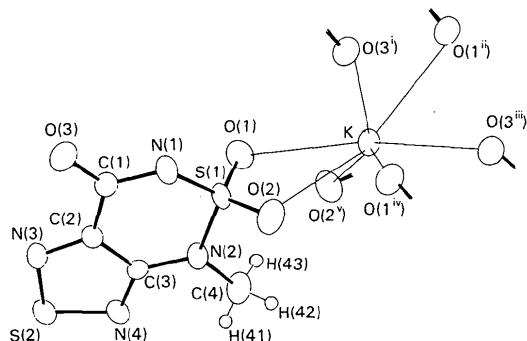


Fig. 1. Perspective drawing of the structure (Johnson, 1965). Some symmetrically related atoms are also shown. Thermal ellipsoids scaled to 50% probability. For symmetry code see Table 2.

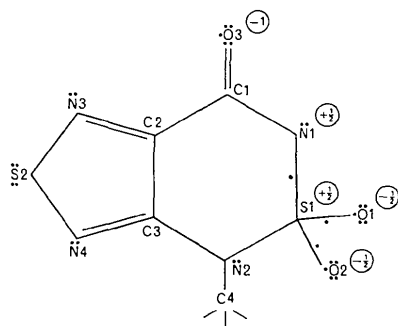


Fig. 2. Major electron distribution model according to Linnett (1966).

Each K^+ ion is surrounded by seven O atoms forming a very distorted laterally capped trigonal prism, with distances ranging from 2.72 (4) to 3.10 (1) Å.

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Structure of (L-Alanyl-L-histidinato)copper(II) 3·5-Hydrate, $[Cu(C_9H_{12}N_4O_3)] \cdot 3 \cdot 5H_2O$

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(Received 8 February 1983; accepted 19 September 1983)

Abstract. $M_r = 350.82$, orthorhombic, $P2_12_12$, $a = 10.037$ (7), $b = 14.477$ (10), $c = 9.735$ (7) Å, $V = 1414$ Å³, $Z = 4$, $D_x = 1.647$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 1.43$ mm⁻¹, $F(000) = 727$, room temperature, $R = 0.045$ for 1588 unique observed reflections. The Cu atom is four-coordinated. The four closest

donor atoms are the amino, peptide and imidazole N atoms of one peptide and a carboxyl O of another. They form an approximate square-planar arrangement around the Cu atom. The Cu atom also interacts weakly with the second O atom of the carboxyl group to which it is bonded. The polymeric Cu–dipeptide–

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