

Potassium Thyminate Trihydrate, $K(C_5H_5N_2O_2) \cdot 3H_2O$

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Abstract

$K(C_5H_5N_2O_2) \cdot 3H_2O$, monoclinic, $P2_1/c$, $Z = 4$, $a = 11.676$ (3), $b = 6.572$ (2), $c = 13.072$ (2) Å, $\beta = 110.24$ (2)°, $V = 941.1$ (4) Å³, $D_c = 1.54$, $D_o = 1.55$ (1) Mg m⁻³. The structure was determined by direct methods and refined to $R_w = 0.063$. The dimensions of the thyminate ion differ significantly from those of thymine only in the internal ring angles at the deprotonated N atom (5.6° smaller) and adjacent C atoms (5.2 and 3.2° larger). The crystal is held together by an extensive hydrogen-bonding network involving the water molecules.

Introduction

The title compound was prepared by reaction of equivalent amounts of thymine and KOH in a small amount of water. After filtration of the solution, evaporation to dryness and stirring for half an hour in excess dimethylformamide at 363 K, the salt was filtered off and dried under high vacuum. $K(C_5H_5N_2O_2)$: calculated C 36.6, H 3.1, N 17.1%; found C 36.7, H 3.2, N 16.9%. By recrystallizing the anhydrous salt from H₂O (1 g/3 ml H₂O) the trihydrate was obtained: $K(C_5H_5N_2O_2) \cdot 3H_2O$: calculated C 27.4, H 5.1, N 12.9%; found C 27.6, H 5.2, N 12.8%. The colourless crystals were corner-truncated prisms. A crystal, which was homogeneous under the polarizing microscope, was cut to a rough needle and ground to a cylinder of dimensions $r = 0.1$, $l = 0.3$ mm. Since the crystals showed evidence of slow decomposition in air, the crystal used for X-ray studies was sealed in a fused-quartz capillary. Photographs showed the systematic absences of the space group $P2_1/c$. The cell was determined by a least-squares fit of 15 well centred reflections ($20^\circ < 2\theta < 34^\circ$) on a Syntex $P2_1$ diffractometer and the density was determined by flotation in a dichloromethane–carbon tetrachloride mixture yielding $Z = 4$ for the title formula. The intensities of 2468 independent reflections up to $2\theta =$

55° were measured with Mo $K\alpha$ radiation. The computer-controlled Syntex $P2_1$ diffractometer was operated in a $2\theta(\text{counter})-\theta(\text{crystal})$ scan mode with a crystal monochromator. After removal of systematically absent reflections and those for which $I \leq 0$, 936 reflections were considered observed [$I > 3.0\sigma(I)$] and were used for the structure determination; 941 were considered unobserved and were given no weight in the structure determination unless $F_c > F_o$.* The method of data treatment has been described previously (Hughes, Krishnamachari, Lock, Powell & Turner, 1977; Lippert, Lock, Rosenberg & Zvagulis, 1977). No correction was made for absorption ($\mu = 0.055$ mm⁻¹, μR min. = 0.11, μR max. = 0.17) but a correction was made for extinction (Larson, 1967; $g = 1.25 \times 10^{-6}$). The stability of the experimental system was monitored by measuring two standard reflections after every 48 reflections (214, 122̄). They showed an e.s.d. of 1.78% with no time variation.

The phase problem was solved by direct methods using 54 reflections with $|E| > 1.35$ and 14 sets of starting phases. A subsequent E map with the most reliable set of phases yielded all the non-hydrogen atoms. Full least-squares refinement, using anisotropic temperature factors for the non-hydrogen atoms and minimizing $\sum w(|F_o| - |F_c|)^2$, followed by a Fourier difference synthesis, revealed the H atoms. These were included in the final refinements. The H atoms were given isotropic temperature factors 20% greater than the atoms to which they were attached and these temperature factors were not refined. Statistical tests (Hamilton, 1965) were applied for each increase in the number of variables. Convergence was obtained with 152 variables at $R = 0.059$ (0.064) and $R_w = 0.044$ (0.063) for the observed (all) reflections with a final maximum shift/error of 0.30. The weighting scheme applied was $1/w = \sigma_F^2 + (0.03F_o)^2$;† scattering factors

* The large number of unobserved reflections occurred mainly for $2\theta > 30^\circ$.

† The value 0.03 was chosen to make $\langle w(|F_o| - |F_c|)^2 \rangle$ locally independent of F_o and $\sin \theta/\lambda$.

Table 1. *Positional parameters for potassium thyminate trihydrate*

	x	y	z
K	0.0281 (1)	0.2635 (2)	0.4175 (1)
N(1)	0.3219 (4)	0.0284 (6)	0.2964 (3)
C(2)	0.3097 (4)	0.2079 (8)	0.3392 (4)
O(2)	0.2087 (3)	0.2921 (5)	0.3249 (3)
N(3)	0.4131 (4)	0.3076 (6)	0.4024 (3)
H(3)	0.407 (6)	0.41 (1)	0.429 (5)
C(4)	0.5304 (4)	0.2402 (8)	0.4247 (4)
O(4)	0.6170 (3)	0.3447 (6)	0.4847 (3)
C(5)	0.5415 (4)	0.0505 (8)	0.3775 (4)
C(51)	0.6658 (6)	-0.036 (1)	0.3959 (5)
H(51)	0.696 (7)	0.02 (1)	0.348 (6)
H(52)	0.658 (6)	-0.19 (1)	0.369 (6)
H(53)	0.701 (6)	-0.03 (1)	0.459 (6)
C(6)	0.4368 (5)	-0.0423 (9)	0.3180 (4)
H(6)	0.447 (6)	-0.18 (1)	0.283 (6)
O(1)	0.8517 (3)	0.2151 (7)	0.2085 (3)
H(101)	0.785 (7)	0.30 (1)	0.198 (6)
H(102)	0.815 (7)	0.13 (1)	0.183 (6)
O(3)	0.0216 (4)	0.3418 (7)	0.1183 (3)
H(301)	0.085 (7)	0.31 (1)	0.170 (6)
H(302)	-0.035 (7)	0.31 (1)	0.138 (6)
O(5)	0.8246 (4)	0.4576 (7)	0.4353 (3)
H(501)	0.762 (6)	0.40 (1)	0.453 (6)
H(502)	0.786 (6)	0.48 (1)	0.370 (6)

were taken from Cromer & Waber (1974) and correction for anomalous scattering was applied to all atoms except H (Cromer, 1974). The final positional parameters of all atoms are given in Table 1.* All calculations were carried out on a CDC 6400 computer.†

Discussion

The monoanions of thymine and uracil exist in solution in two tautomeric forms, namely the N(1) and N(3) deprotonated forms (Wierzchowski, Litonska & Shugar, 1965; Wittenberg, 1966; Lippert, 1979). Because of the solvent dependency of the tautomer equilibrium, it should, in theory, be possible to obtain metal complexes of the individual tautomers by choosing the 'right' solvent (Lippert, 1979). Nevertheless only N(1)-bonded thyminato complexes have been characterized so far (Kistenmacher, Sorrell & Marzilli, 1975; Faggiani, Lippert & Lock, 1979; Faggiani, Lippert, Lock & Pfab, 1979; Lippert, Neugebauer &

Pfab, 1979). If, however, N(1) is blocked, as in the 1-methylthyminate anion, coordination occurs through N(3) (Kosturko, Folzer & Stewart, 1974) or even to two Pt atoms through N(3) and O(4) (Lock, Peresie, Rosenberg & Turner, 1978). In this latter case the C(2)—O(2) and C(4)—O(4) distances are significantly different although no such difference was observed when Pt was bonded to N(1) (Faggiani, Lippert & Lock, 1979). The two distances are not significantly different in thymine (Gerdil, 1961). It was of interest to see whether any difference in C—O bond lengths exists in the free anion or whether it arises from the coordination of the Pt atoms.

Thus we have examined potassium thyminate trihydrate by single-crystal X-ray diffraction. The result of this study was unexpected in that the thyminate ligand exists in the N(1)-deprotonated form in the solid state, whereas from considerations concerning the polarity of the individual tautomers one might have expected the more polar N(3)-deprotonated form to dominate (Lippert *et al.*, 1979). We suspect that factors of solubility and hydrogen bonding are of importance in deciding which tautomer is present in the potassium salt.

The thyminate anion is illustrated in Fig. 1 and bond lengths and bond angles are shown in Tables 2 and 3 together with corresponding data for thymine monohydrate (Gerdil, 1961).* The C—O bond lengths are not significantly different. In addition, although the mean values of the C—O distances are greater than in neutral thymine, the errors are such that there is no significance in the differences. Indeed, none of the corresponding pairs of bond lengths differs significantly between thymine and the thyminate anion.

* Although the structures of thymine and thymine-*p*-benzoquinone have been determined (Ozeki, Sakabe & Tanaka, 1969; Sakurai & Okunuki, 1971) they are not particularly accurate and we have used the more accurate work of Gerdil (1961) for comparison.

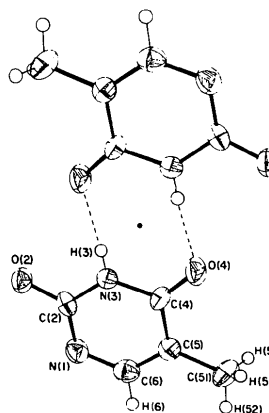
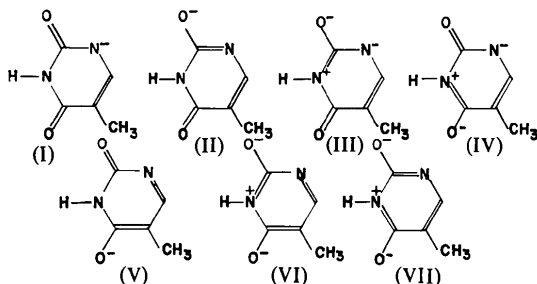


Fig. 1. The thyminate anion showing the hydrogen bonding to an anion related by the centre of symmetry at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ to give a *T-T* pair.

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34476 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† Most programs used were from the XRAY package (Stewart, 1976). The direct-methods program was from the *SHELX* package (Sheldrick, 1976) and the full-matrix least-squares program *CUDLS* was used (J. S. Stephens). The diagrams were prepared using *ORTEP* II (Johnson, 1976).

Nevertheless, some electronic rearrangement has taken place, since the internal angle at deprotonated N(1) has decreased significantly (8.8σ) compared to the corresponding angle in thymine, while the adjacent internal angles at C(2) and C(6) have increased (5.0σ and 7.4σ respectively). This change of the internal angles upon protonation has been noticed previously (Singh, 1965). The thyminate anion can be treated in terms of resonance structures in a manner similar to that of Gerdil (1961). The forms considered were



Calculations using a Pauling (1960) relationship for bond lengths and bond orders and based on values of single- and double-bond lengths quoted by Gerdil (1961), with resonance corrections of 0.03 \AA for C—C, 0.04 \AA for C—N and 0.05 \AA for C—O, gave (I), 14%; (II), 25%; (III), 11%; (IV), 12%; (V), 24%; (VI), 7%. The calculated bond lengths are shown in Table 2 and it can be seen that there is excellent agreement with experimental values. The net charges on the various atoms are [thymine in parentheses (Gerdil, 1961)] N(1), 0.37^- (0.39^+); N(3), 0.37^+ (0.35^+); O(2), 0.50^- (0.42^-); O(4), 0.50^- (0.32^-). The net effect of the removal of the proton from N(1) is to change it from a positive to a negative centre, but a significant amount of charge (0.24^-) has been delocalized on to the O atoms giving equal charge to both.

Table 2. Bond distances (\AA) within the thyminate anion

	This work	Thymine monohydrate*	Calculated
N(1)—C(2)	1.334 (7)	1.355 (9)	1.338
C(2)—O(2)	1.256 (6)	1.234 (7)	1.254
C(2)—N(3)	1.372 (6)	1.361 (8)	1.373
N(3)—H(3)	0.78 (7)	0.81	—
N(3)—C(4)	1.371 (6)	1.391 (6)	1.373
C(4)—O(4)	1.249 (5)	1.231 (8)	1.251
C(4)—C(5)	1.417 (7)	1.447 (9)	1.427
C(5)—C(51)	1.497 (8)	1.503 (8)	—
C(51)—H(51)	0.90 (9)	0.97	—
C(51)—H(52)	1.04 (8)	0.88	—
C(51)—H(53)	0.79 (7)	0.80	—
C(5)—C(6)	1.346 (7)	1.349 (9)	1.348
C(6)—H(6)	1.02 (8)	0.86	—
C(6)—N(1)	1.355 (7)	1.382 (7)	1.341

* Gerdil (1961).

Table 3. Interatomic angles ($^\circ$) within the thyminate anion

	This work	Thymine monohydrate*
N(1)—C(2)—O(2)	123.9 (4)	122.7
N(1)—C(2)—N(3)	118.4 (4)	115.2
O(2)—C(2)—N(3)	117.7 (5)	122.1
C(2)—N(3)—H(3)	119 (5)	108
C(2)—N(3)—C(4)	125.5 (4)	126.3
H(3)—N(3)—C(4)	115 (4)	125
N(3)—C(4)—O(4)	119.2 (5)	118.3
N(3)—C(4)—C(5)	115.3 (4)	115.6
O(4)—C(4)—C(5)	125.5 (4)	126.1
C(4)—C(5)—C(51)	119.5 (4)	119.0
C(4)—C(5)—C(6)	116.6 (5)	118.2
C(5)—C(51)—H(51)	110 (5)	126
C(5)—C(51)—H(52)	110 (4)	123
C(5)—C(51)—H(53)	106 (6)	118
H(51)—C(51)—H(52)	98 (7)	96
H(51)—C(51)—H(53)	122 (7)	96
H(52)—C(51)—H(53)	111 (6)	89
C(51)—C(5)—C(6)	123.9 (5)	122.8
C(5)—C(6)—H(6)	115 (4)	127
C(5)—C(6)—N(1)	127.0 (5)	121.8
H(6)—C(6)—N(1)	117 (4)	111
C(6)—N(1)—C(2)	117.2 (4)	122.8

* Gerdil (1961). E.s.d.'s for angles not involving hydrogen are $0.3\text{--}0.5^\circ$. Other errors not given.

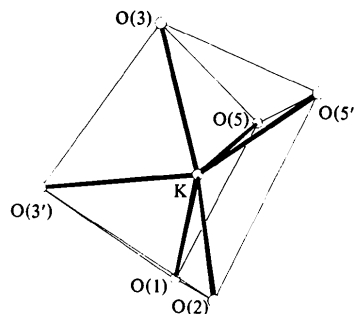


Fig. 2. The coordination of the K atom showing the distorted trigonal-prismatic arrangement.

The environment of the K ion is shown in Fig. 2. The ion is surrounded by six O atoms at about 2.8 \AA . The only other atoms closer than 3.5 \AA are the H atoms of the water molecules. The O atoms form a very distorted trigonal prism around the K ion. The most noticeable distortions are the long triangular edges [O(2)—O(1) 3.94 , O(5)—O(5') 3.89 , O(2)—O(3) 4.23 \AA]. The O(2)—O(1) distance is longer than normal because of the hydrogen bonding of each of these atoms to an O(3) water molecule. Similarly the nearest approach of O(5) and O(5') is constrained by hydrogen bonding to N(1) and O(4). O(2)—O(3) is long because of the steric requirements of an adjacent O(3) group bonded to O(2) through an O(1) water molecule.

Table 4. *Hydrogen-bonding distances (Å) and angles (°) ($X-H \cdots Y$)*

$X-H \cdots Y$	$X-Y$	$X-H$	$H \cdots Y$	$\angle X-H \cdots Y$
N(3)—H(3)···O(4)	2.807 (6)	0.78 (7)	2.04 (7)	171 (8)
O(1)—H(101)···N(1)	2.874 (6)	0.92 (8)	1.99 (8)	163 (5)
O(1)—H(102)···O(2)	2.864 (6)	0.73 (8)	2.22 (8)	148 (7)
O(3)—H(301)···O(2)	2.845 (5)	0.85 (6)	2.04 (7)	159 (8)
O(3)—H(302)···O(1)	2.765 (7)	0.81 (10)	1.96 (10)	169 (7)
O(5)—H(501)···O(4)	2.815 (6)	0.92 (8)	1.92 (8)	166 (7)
O(5)—H(502)···N(1)	2.955 (5)	0.83 (7)	2.13 (7)	177 (9)

Other angles

H(101)—O(1)—H(102)	93 (7)	H(301)—O(3)—H(302)	105 (8)
H(501)—O(5)—H(502)	97 (7)	C(2)—N(3)—H(3)	119 (5)
C(4)—N(3)—H(3)	115 (5)	C(2)—N(1)—H(502)	117 (2)
C(6)—N(1)—H(502)	111 (2)	C(2)—N(1)—H(101)	120 (2)
C(6)—N(1)—H(101)	109 (2)	H(101)—N(1)—H(502)	76 (3)
C(2)—O(2)—H(301)	118 (2)	C(2)—O(2)—H(102)	123 (2)
H(102)—O(2)—H(301)	82 (3)	H(3)—O(4)—H(501)	144 (3)
H(101)—O(1)—H(302)	114 (6)	H(102)—O(1)—H(302)	116 (8)
C(4)—O(4)—H(3)	123 (2)	C(4)—O(4)—H(501)	123 (2)

Hydrogen bonding (Table 4) is of prime importance in holding the thymine bases together. As can be seen in Fig. 1 the thymine ions are held as 'base pairs' through N(3)—H(3)···O(4) bonds. In addition, O(4) in any base pair is bonded through the water molecule H(501)—O(5)—H(502) to N(1) in an adjacent base pair related by the 2_1 operation. Similarly N(1) in a molecule is also bonded through H(101)—O(1)—H(102) to O(2) in a molecule related to the former by the unit translation along b ; in addition O(1) is bonded through H(302)—O(3)—H(301) to another O(2) atom in a molecule related to that containing the first O(2) atom by the 2_1 operation and an a translation. O or N atoms involved in hydrogen bonding, except N(3) and O(4), can be considered as interacting with four other atoms, which form a very rough tetrahedron about the central atom, although some of the interactions may be covalent or ionic. These are

Central atom	Interacting atoms/ions
O(1)	H(101), H(102), H(302), K^+
O(3)	H(301), H(302), K^+ , K^+
O(5)	H(501), H(502), K^+ , K^+
N(1)	H(101), H(502), C(2), C(6)
O(2)	H(102), H(301), C(2), K^+
N(3)	H(3), C(2), C(4)
O(4)	H(3), H(501), C(4).

This is consistent with Brown's (1976) model of hydrogen bonding, as are the hydrogen-bond lengths and angles.

The packing in the unit cell is shown in Fig. 3. The hydrogen-bonded base pairs form the basis of the structure, being arranged in layers parallel to the bc plane, centred at $x = \frac{1}{2}$. A given pair of bases is tilted with respect to the b axis so that pairs of bases related by the b translation overlap like tiles on a roof. In the c direction the pairs of bases are related by the c glide so that each subsequent pair of bases is tilted in the

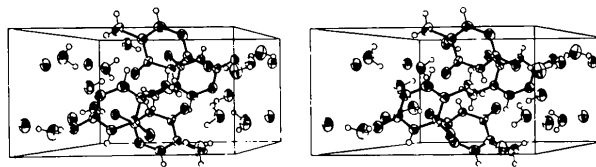


Fig. 3. Stereogram (stereoscopic pair of perspective projections) of potassium thyminate trihydrate showing the contents of one unit cell. a and b are horizontal and vertical respectively, and the view is down c^* .

opposite direction to adjacent pairs. Contact between adjacent pairs is primarily between the methyl group and H(6) on one base with the π cloud and the C(4)—C(5) bond of a base in an adjacent pair. The hydrogen-bonding network holding the base layer together orients the water molecules such that the O atoms point towards the $x = 0$ plane. The packing in the a direction is then primarily an ion-dipole interaction between these external O atoms of the base layer and the K ions which lie close to $x = 0$.

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The Crystal Structures of the Room- and Low-Temperature Modifications of Tris(η -cyclopentadienyl)-di- μ_3 -thio-tricobalt, $[\text{Co}_3(\eta\text{-C}_5\text{H}_5)_3\text{S}_2]$

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Abstract

The crystal structures of the title compound at room temperature and at 130 K are determined. The room-temperature modification is hexagonal, $P6_3/m$, with $a = 9.413(2)$, $c = 10.094(4)$ Å and $Z = 2$, and is isostructural with $[\text{Ni}_3(\eta\text{-C}_5\text{H}_5)_3\text{S}_2]$ [(Vahrenkamp, Vernon, Uchtman & Dahl (1968). *J. Am. Chem. Soc.* 90, 3272–3273)], except for the mode of statistical distribution of the η -cyclopentadienyl rings. The Co–Co distance is 2.691 Å which is definitely longer than those of most of the other trinuclear cobalt complexes, and this difference is explained by the Cotton–Haas theory of metal–metal bonding. The low-temperature modification is also hexagonal with $a = 16.080(2)$, $c = 29.886(2)$ Å and $Z = 18$; this is a superstructure of the room-temperature modification and the symmetry can be given by the *Mischgruppe* $P6_1 \cup p3^\circ$. The trigonal bipyramid comprising Co_3S_2 is no longer regular and the three η -cyclopentadienyl rings take three definite orientations.

Introduction

Tris(η -cyclopentadienyl)-di- μ_3 -thio-tricobalt, $[\text{Co}_3(\eta\text{-C}_5\text{H}_5)_3\text{S}_2]$, was first prepared by Otsuka, Nakamura & Yoshida (1968). They also found that this complex is paramagnetic at room temperature and becomes dia-

magnetic below 192.5 K. Sorai, Kosaki, Suga, Seki, Yoshida & Otsuka (1971) interpreted the mechanism of the phase transition in terms of the cooperative coupling between the orientational motion of the η -cyclopentadienyl rings (hereafter Cp rings) and the electronic states of the molecule. In this paper, the crystal structures of the title compound at room temperature and at 130 K are reported.

Determination of the crystal structure of the room-temperature modification

Crystals of tris(η -cyclopentadienyl)-di- μ_3 -thio-tricobalt were kindly provided by Professor Otsuka. They are hexagonal platelets or slender needles, dark brown in color. Weissenberg and oscillation photographs showed the dihexagonal symmetry $6/mmm$. The systematic extinctions were observed only for $00l$ with l odd, corresponding to the space group $P6_322$, but it was soon found that the crystal consisted of twins, as will be described later. A crystal approximately $0.2 \times 0.2 \times 0.3$ mm was used for X-ray data collection on a Rigaku four-circle diffractometer. The crystal data are given in Table 1. The cell parameters were determined with Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å) by a least-squares fit of 15 reflexions in the range $40^\circ \leq 2\theta \leq 50^\circ$. The estimated standard deviations of the cell parameters are those from the least-squares calculations.