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Crystallography of Metal Picrates.

I. General Survey. Crystal Structure of Red Thallium(I) Picrate $\text{TlC}_6\text{H}_2\text{N}_3\text{O}_7$

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The red polymorph of Tl^{I} picrate is monoclinic, $a = 10.610(1)$, $b = 4.548(5)$, $c = 19.148(2)$ Å, $\beta = 101.1(1)^\circ$, $Z = 4$, space group $P2_1/c$. Intensities were measured on a Weissenberg diffractometer. The structure was refined to $R = 11.7\%$. There are columns of Tl^{I} ions along the $[010]$ direction, each column being surrounded by four stacks of picrate ions. Each Tl^{I} ion is surrounded by nine O atoms, six at the vertices of a distorted trigonal prism and three capped on the three rectangular faces (shortest $\text{Tl}^{\text{I}} \cdots \text{O} = 2.83$ Å). Similar (but not identical) coordination polyhedra have been reported in cryptate complexes of Tl^{I} and alkali-metal salts. We conclude that the $6s^2$ lone pair is not stereochemically active in red Tl^{I} picrate.

Introduction

Picric acid forms salts with many organic (Gartland, Freeman & Bugg, 1974) and metallic cations. Anhydrous picrates are formed with K^+ , Rb^+ , NH_4^+ , Cs^+ , Tl^+ and Ag^+ while picrates with various degrees of hydration are formed by other metals such as Li, Na, the alkaline earths, Zn, Cd, Hg, various transition metals, Al, Y, Sc, In and various rare-earth metals (Tucholski, 1932, 1933, 1934*a,b,c*). Crystal structures have been reported for the isomorphous NH_4 (Beukelman & Donnay, 1950; Maartman-Moe, 1969) and K picrates (Bettman & Hughes, 1954; Maartman-Moe, 1969; Palenik, 1972) and for some organic

picrates [see, for example, Gartland *et al.* (1974), who give earlier references].

Tl^{I} picrate has two polymorphic forms, whose thermodynamic relation has been studied by solubility measurements (Rabe, 1901). The red polymorph, stable at 25°C , has been reported, correctly, as monoclinic and the yellow polymorph, metastable at 25°C , incorrectly, as triclinic (Stevanovic, 1903). The phase transformation has been studied by Cohen & Moesveld (1920) (see also Cohen, 1929). While the equilibrium temperature of red \rightleftharpoons yellow is 46°C (Rabe, 1901) or 44°C (Cohen, 1929), the transformation red \rightarrow yellow proceeds very sluggishly below 120°C . Study of the phase transformation must be based on knowledge of

the crystal structures of the two polymorphic forms. In this paper we report crystal data for the picrates of Tl, Rb and Cs and the crystal structure of red Tl^I picrate. Work is in progress on the structure of the yellow polymorph and the nature of the phase transformation.

General survey

Crystal data are summarized in Table 1. There are three structure types: the isomorphous NH₄ and K picrates; the isomorphous Rb, Cs and red Tl^I picrates (this isomorphism was noted by Stammer, 1968) and yellow Tl^I picrate. The crystallographic results are in accordance with Stammer's (1968) findings that Rb and Cs picrates form a one-phase system at all compositions, whereas K and Cs picrates have a large miscibility gap. DTA measurements show that K, Rb and Cs picrates undergo phase transformations at 250, 243 and 280 °C respectively (Stammer, 1968); the structures of these high-temperature polymorphs are not known.

Crystal structure of red Tl^I picrate

Measurement and correction of intensities

An approximately rectangular prism 0.3 × 0.2 × 0.2 mm was mounted about **b** on a Stoe semi-automatic Weissenberg diffractometer. Intensities of 2247 reflexions (*h0l* to *h4l*) were measured by the $\omega/2\theta$ method with graphite-monochromated Mo *K* α radiation (scan width 2.4° 2 θ , backgrounds counted for 20 s at the extrema of the scan). Geometrical and absorption corrections (Busing & Levy, 1957) were applied.

Structure determination and refinement

The position of the Tl ion was found from a Patterson synthesis, and the positions of all the other non-hydrogen atoms from a difference synthesis. Atomic parameters were refined by least squares, with anisotropic Debye–Waller factors for all atoms. H atoms were ignored. The weighting scheme was $w = 1/25$ for $|F_o| \leq 25$, $w = 1/|F_o|$ for $|F_o| > 25$. The scattering factors were taken from *International Tables for X-ray Crystallography* (1962) as follows. Tl: Table 3.3.1B, p. 212; dispersion corrections for real and imaginary parts of the scattering factor from Table 3.3.2C, pp. 215–216. O, N, C: Table 3.3.1A, pp. 202–203.

Refinement was stopped at $R = 0.14$ and goodness of fit = 1.19. These values are for 2247 measured reflexions; when the 240 reflexions with $F_o = 0$ are removed from the list, $R = 0.117$. Furthermore some 50 of the lower-angle reflexions showed discrepancies of 20% or more between observed and calculated values of the structure factors; these could be due to measurement errors, extinction or inaccurate absorption corrections (transmission factors ranged from 0.003 to 0.120). It was considered that further refinement was not warranted without remeasurement of the intensities from a very small spherical crystal. The anisotropic Debye–Waller factors cannot have much physical significance because of the large absorption corrections. Furthermore the absolute values of β_{33} are not established because the interlayer scale factors were not measured experimentally (Lingafelter & Donohue, 1966). The final atomic parameters are given in Table 2 (see Fig. 3 for atomic numbering).*

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32085 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Crystal data for various metal picrates* M(C₆H₂N₃O₇)

Compound	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β (°)	Space group	<i>Z</i>	Density g cm ⁻³		Volume of unit cell (Å ³)	Notes
							Measured	Calculated		
NH ₄ picrate	13.45	19.74	7.12	—	<i>Ibca</i>	8	1.78	1.71	1890	1
K picrate	13.33	19.09	7.14	—	<i>Ibca</i>	8	1.93	1.96	1894	1
Rb picrate	9.55	4.60	21.32	100.8	<i>P2₁/c</i>	4	2.30	2.26	920.0	2
Cs picrate	9.74	4.71	21.71	102.4	<i>P2₁/c</i>	4	2.49	2.47	972.6	2
Tl picrate* (red)	10.610 (1)	4.548 (5)	19.148 (2)	101.1 (1)	<i>P2₁/c</i>	4	3.164	3.166	907.04	2, 3, 4
Tl picrate (yellow)	15.42 (1)	15.866 (4)	3.946 (5)	91.06 (10)	<i>P2₁/a</i>	4	2.993	2.993	959.51	2, 3, 5

Notes: (1) Results from Maartman-Moe (1969). (2) This research. (3) Densities (17 °C) from Rabe (1901). (4) Stevanovic (1903) gives $a:b:c = 2.1118:1.2.3345$; $\beta = 100^\circ 58'$ (present work $a:b:c = 4.2102:1.2.3329$). The agreement is excellent if Stevanovic's *a* axis is doubled. (5) Stevanovic gives $a:b:c = 1.0566:1.0.5126$, $\alpha = 91^\circ 5'$, $\beta = 104^\circ 4'$, $\gamma = 89^\circ 4'$.

* F.W. 432.46, $\mu(\text{Mo } K\alpha) = 179.4 \text{ cm}^{-1}$. Cell dimensions by back-reflexion Weissenberg and Mathieson inclined-beam oscillation method (Herbstein, 1963), with Cu *K* α radiation ($\lambda K\alpha_1 = 1.54040 \text{ \AA}$, $\lambda K\alpha_2 = 1.54434 \text{ \AA}$).

Table 2. *Final atomic parameters ($\times 10^4$) and their e.s.d.'s for non-hydrogen atoms*

The atoms in this table are referred to in the text as the 'reference atoms'. The anisotropic Debye-Waller factors are defined by $T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{23}kl + 2\beta_{13}hl)]$.

	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Tl	-978.6 (10)	-235 (2)	1405.6 (6)	56 (1)	306 (7)	29 (0)	-25 (2)	10 (0)	11 (1)
C(1)	1959 (16)	3162 (46)	1458 (12)	33 (13)	123 (105)	22 (6)	-37 (25)	1 (7)	4 (18)
C(2)	2507 (24)	4145 (66)	829 (10)	78 (22)	464 (170)	4 (4)	-92 (48)	-9 (8)	50 (20)
C(3)	3582 (17)	3074 (48)	655 (10)	28 (14)	305 (117)	8 (4)	-55 (28)	8 (6)	-44 (16)
C(4)	4363 (23)	1128 (58)	1112 (15)	61 (20)	206 (138)	30 (8)	37 (35)	21 (10)	-6 (23)
C(5)	3897 (21)	89 (47)	1692 (12)	34 (17)	258 (132)	8 (5)	-43 (29)	-12 (7)	3 (17)
C(6)	2766 (16)	895 (47)	1848 (10)	2 (13)	265 (107)	13 (5)	-25 (25)	10 (6)	19 (16)
N(1)	1666 (17)	5923 (43)	300 (10)	39 (15)	110 (97)	22 (6)	-67 (26)	-2 (7)	-14 (16)
N(2)	5537 (21)	132 (42)	942 (13)	56 (18)	102 (114)	27 (6)	30 (27)	16 (8)	-42 (18)
N(3)	2400 (20)	-492 (46)	2455 (10)	61 (18)	308 (114)	12 (5)	-8 (32)	17 (7)	29 (16)
O(1)	1083 (23)	8039 (53)	523 (13)	141 (26)	295 (128)	45 (9)	72 (44)	22 (12)	16 (25)
O(2)	1612 (28)	5422 (44)	-304 (12)	134 (32)	207 (106)	22 (6)	-14 (40)	-24 (11)	14 (19)
O(3)	5994 (18)	1622 (47)	480 (10)	74 (17)	469 (123)	21 (5)	-40 (35)	32 (8)	-14 (19)
O(4)	6047 (14)	-2068 (39)	1251 (9)	42 (12)	208 (94)	25 (5)	4 (24)	-7 (6)	3 (16)
O(5)	3155 (23)	-2369 (57)	2773 (12)	118 (23)	634 (156)	30 (7)	33 (49)	29 (10)	44 (26)
O(6)	1335 (19)	106 (45)	2614 (11)	57 (16)	598 (140)	19 (6)	34 (31)	14 (8)	-34 (19)
O(7)	926 (13)	4187 (41)	1589 (10)	21 (11)	328 (94)	34 (6)	-20 (23)	16 (6)	-22 (18)

Table 3. *Dimensions of coordination polyhedron of oxygen atoms about the Tl⁺*

Values of $d(\text{O} \cdots \text{O}) > 3.5 \text{ \AA}$ have been omitted. The atoms are numbered in accordance with Fig. 2, and defined on the left-hand side of the table according to the ORTEP conventions. The symmetry operations produce the following relations among the atomic coordinates: 01 $\bar{x}yz$; 02 xyz ; 03 $x, \frac{1}{2} + y, \frac{1}{2} - z$; 04 $x, \frac{1}{2} - y, \frac{1}{2} + z$.

Definition of oxygen atoms	Distances between atoms (Å)									
	Tl	1	2	3	4	5	6	7	8	9
O(3) 55502	1									
O(7) 54501	2	62								
O(6) 54503	3	81	61							
O(2) 56502	4	95	134	160						
O(7) 55501	5	132	97	128	68					
O(6) 55503	6	161	134	98	80	63				
O(1) 54501	7	62	51	111	84	72	134			
O(6) 55501	8	126	64	74	122	54	71	83		
O(4) 45501	9	70	113	68	92	149	92	132	136	

Angles $X-\text{Tl}-Y(^{\circ})$

Angles ($^{\circ}$) defining the distorted trigonal prism of oxygens about the Tl⁺ ion (see Fig. 2)

$\angle 1\ 2\ 3$	76	$\angle 2\ 3\ 6$	98
$\angle 2\ 1\ 3$	50	$\angle 1\ 2\ 5$	87
$\angle 1\ 3\ 6$	93		

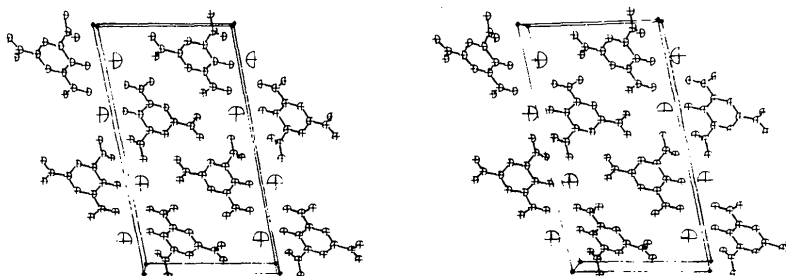


Fig. 1. ORTEP (Johnson, 1965) stereodiagram of the unit-cell contents ([010] normal to the page). Hydrogen atoms have been omitted.

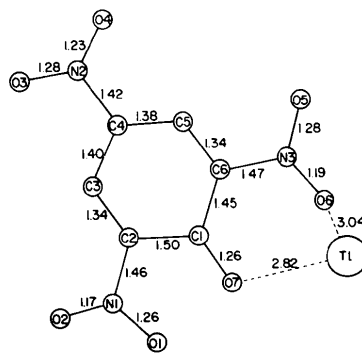
Description of the structure

The crystal structure (Fig. 1), which is different from that of K picrate, is based on columns of translationally equivalent Tl^+ ions arranged along [010], each such column being surrounded by four stacks of parallel, translationally equivalent picrate ions; the stack axes are along [010] and the planes of the benzene rings of the picrate ions are inclined at 43° to the (010) plane. Each Tl^+ ion is surrounded by nine O atoms (Table 3) from seven different picrate ions.

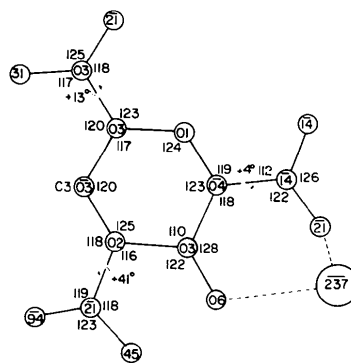
The coordination polyhedron about Tl^+ is shown in Fig. 2; the six nearest O atoms of a particular Tl^+ ion are arranged about the ion in a distorted trigonal prism. The principal distortion is that the sides of the prism are almost rectangular rather than square – the height is always 4.55 \AA but the widths are 3.11 , 3.29 and 3.95 \AA and the angles are 98 , 87 and 93° . The top and bottom triangular faces are congruent since they are related by translation along [010]. Such congruence is not found in some of the metal cryptates discussed below, where there is a mutual rotation of these triangular faces towards the trigonal antiprismatic configuration. Each of the rectangular faces is capped by an O atom, with $Tl^+ \cdots O$ distances not very different from those found within the trigonal prism. The triangular faces are capped by Tl^+ ions, 4.55 \AA above and below the reference Tl^+ ion. The $Tl^+ \cdots O$ distances accepted as significant in this description range from 2.83 (to the phenoxide O in the reference picrate ion) to 3.22 \AA . There are four other O atoms within 4 \AA of the reference Tl^+ ion (at 3.35 , 3.46 , 3.80 and 3.84 \AA) which have been omitted from this description because of their smaller contributions to the cohesion of the crystal.

The dimensions of the picrate ion (Fig. 3) are compatible with the much more accurate values found, for example, in tryptamine picrate and DL-tryptophan picrate methanolate (Gartland *et al.*, 1974); thus detailed discussion here is not warranted. The benzene ring of the picrate ion is planar; the equation of its plane with respect to the crystal axes is (X, Y, Z in Å) $0.3910X + 0.7351Y + 0.4691Z = 3.152 \text{ \AA}$. The nitro

groups are twisted out of this plane by $+41^\circ$ [$N(1) O(1) O(2)$], $+13^\circ$ [$N(2) O(3) O(4)$] and $+4^\circ$ [$N(3) O(5) O(6)$]. The first and last of these nitro groups are also tilted down out of the plane of the benzene ring. [The various planes and interplanar angles were calculated by the methods of Schomaker, Waser, Marsh & Bergman (1959) and Waser, Marsh & Cordes (1973).]



(a)



(b)

Fig. 3. Formula unit projected onto plane of benzene ring. Atomic coordinates are listed in Table 2; hydrogen atoms have been omitted. (a) Numbering of atoms, and bond lengths (e.s.d. $\sim 0.02 \text{ \AA}$). (b) Bond angles (e.s.d. $\sim 2^\circ$), torsion angles of nitro groups and displacements of atoms (10^{-2} \AA) from plane of benzene ring.

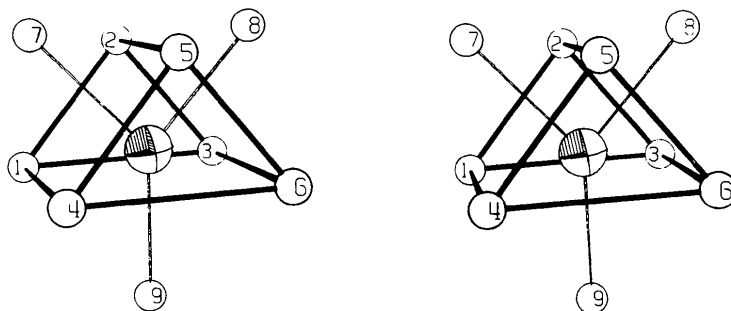


Fig. 2. ORTEP stereodiagram of the coordination polyhedron of oxygen atoms about the Tl^+ ion. The relevant interatomic distances and angles are in Table 3.

Discussion

Discussion of the present results in connexion with the phase transformation will be deferred until the results for the second polymorph are in hand.

The smallest $\text{Tl}^+ \cdots \text{O}$ distance is 2.83 Å, to the phenoxide O atom. If the radius of Tl^+ is 1.49 Å (for c.n. 8) then this would give a radius of 1.34 Å for the phenoxide O, which is reasonable. The ionic radii of Rb^+ and Cs^+ (for c.n. 9) are 1.53 and 1.75 Å and thus one would expect the structure of Rb picrate to resemble that of red Tl^+ picrate more closely than that of Cs picrate. The unit-cell volumes of red Tl^+ , Rb and Cs picrates (Table 1) are in accordance with this expectation.

Tl^+ coordination complexes and salts can be divided into two structural groups, according to whether the $6s^2$ lone pair of the Tl^+ ion is, or is not, stereochemically active. Examples of the first group are salicylato(1,10-phenanthroline)thallium(I) (Hughes & Truter, 1972) and thallos fluoride carbonate (Alcock, 1973). Alcock (1973) has suggested that Tl tetrametaphosphate (Fawcett, Kocman & Nyburg, 1974) also belongs to this group but the coordination around Tl^+ is rather regular and stereochemical activity of the $6s^2$ lone pair does not appear to have been demonstrated unequivocally. The Tl^+ salt of the antibiotic grisorixin, where Tl^+ is coordinated to five O atoms with distances ranging from 2.6–3.0 Å (Alleaume & Hickel, 1972) presumably also belongs to this group.

When the $6s^2$ lone pair is not stereochemically active, Tl^+ behaves structurally like an alkali-metal cation and isomorphism of such Tl^+ salts and complexes with the corresponding Rb and Cs compounds is to be expected. Isomorphism is indeed found in the MX_4 (thiourea) complexes ($\text{M} = \text{K}, \text{Rb}, \text{Cs}, \text{NH}_4, \text{Tl}^+$) (Boeyens & Herbstein, 1967) and in the present series of Rb, Cs and red Tl^+ picrates. We therefore infer that the $6s^2$ lone pair is not stereochemically active in red Tl^+ picrate.

A similar metal–ligand coordination to that encountered here is found in the cryptates of various K, Rb, Cs and Tl^+ salts (Metz, Moras & Weiss, 1971; Moras, Metz & Weiss, 1973*a,b*; Moras & Weiss, 1973). The (222) cryptate ligand is flexible enough for it to wrap itself in the same way around cations of different radii. In these complexes the Na^+ , K^+ , Rb^+ , Ca^+ and Tl^+ ions are all coordinated by six O atoms, at the vertices of a figure intermediate between a trigonal prism and antiprism, with the two triangular faces capped by N atoms. The $\text{Tl}^+ \cdots \text{O}$ distances are all essentially equal at 2.904 (4) Å and the $\text{Tl}^+ \cdots \text{N}$ distance is 2.946 (6) Å, the latter suggesting a covalent interaction which may explain the greater stability of Tl cryptate compared to the others. Moras & Weiss (1973) suggest that the $6s^2$ lone pair of the Tl^+ is directed along the twofold axis of the coordination polyhedron, but this seems un-

likely in view of the similarity of the coordination polyhedra in the various cryptates.

The columns of picrate ions can be considered to be arranged in pleated sheets in the (100) planes, interleaved by analogous sheets composed of the columns of Tl^+ ions. Somewhat similar interleaved pleated sheets of cations and picrate anions are found in pyridinium picrate (Talukdar & Chaudhuri, 1976) and in the monohydrates of guanine and 6-thioguanine picrates (Bugg & Thewalt, 1975). Succinylcholine dipicrate (Jensen, 1975) contains stacks of picrate ions but these are enclosed in channels formed by the flexible cations. In this latter salt the picrate ions are antiparallel in the stacks, and the repeat distance along the stack axis is consequently ~ 7 Å, whereas in the other salts the picrate ions are translationally equivalent (and hence parallel) and the repeat along the stack axis is ~ 4 Å.

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Neutron Diffraction Study of L-Histidine Hydrochloride Monohydrate

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The structure of L-histidine hydrochloride monohydrate has been redetermined by neutron diffraction. 1489 symmetry-independent reflexions have been measured at $\lambda = 1.096 \text{ \AA}$ on a four-circle neutron diffractometer. The structure has been refined to a conventional $R(F^2) = 0.036$ including a treatment for anisotropic extinction. Further data for 183 independent reflexions on a much smaller crystal gave $R(F^2) = 0.026$ by refining scale and extinction factors only. The positions of the heavy atoms are in agreement with a previous X-ray study. The positions of the H atoms have been determined and the hydrogen-bonding scheme is discussed. The histidine molecule adopts the closed form with a planar imidazole group folded back on a planar carboxyl group.

Introduction

Several compounds related structurally to the amino acid histidine have been studied by neutron diffraction. L-Histidine in the orthorhombic modification was reported by Lehmann, Koetzle & Hamilton (1972). The metal-histidine complex bis(L-histidinato)cadmium dihydrate is described by Fuess & Bartunik (1976). The X-ray structure of the orthorhombic form of L-histidine is given by Madden, McGandy & Seeman (1972), that of the monoclinic form by Madden, McGandy, Seeman, Harding & Hoy (1972). The hydrochloride was studied for DL-histidine by Bennett, Davidson, Harding & Morelle (1970) and for L-histidine by Donohue, Lavine & Rollett (1956) and Donohue & Caron (1964) (referred to as DC). The conformation of the histidine molecule in different structures has been discussed by Kistenmacher, Hunt & Marsh (1972) who studied L-N-acetylhistidine monohydrate.

Our present study was begun with two aims: one was a comparison of histidine as the hydrochloride with the conformation as a molecule and in metal-histidine complexes, the other was an evaluation of the modified Laue film technique in neutron diffraction and an estimation of the precision at present available by neutron film techniques. We therefore collected a full data set by the modified Laue technique (Hohlwein, 1975), which was refined in parallel with the data set from the conventional four-circle neutron instrument. The crystal used for the film study had a volume of only 0.3 mm^3 . A full account of this work will be given elsewhere (Hohlwein & Fuess, 1977). In the present paper we shall describe the structure refinement from four-circle data: a complete set from a 4.3 mm^3 crystal and a limited set from the 0.3 mm^3 crystal.

Experimental

The crystals were prepared as a by-product when we tried to prepare rare-earth-histidine crystals intended

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