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Crystal Structure of Hexaurea Salts of Trivalent Metals. I. $\text{Ti}(\text{Urea})_6(\text{ClO}_4)_3$ at Room Temperature

BY B. N. FIGGIS AND L. G. B. WADLEY

School of Chemistry, University of Western Australia, Nedlands, W.A. 6009, Australia

AND J. GRAHAM

C.S.I.R.O., Private Bag, Wembley, W.A. 6014, Australia

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On the basis of 642 independent intensities collected by film techniques the room temperature structure of $\text{Ti}(\text{urea})_6(\text{ClO}_4)_3$ was refined in the space group $R\bar{3}c$ to give a final R of 0.122, omitting unobserved reflections. Hexagonal cell dimensions are $a = 18.132$ (5), $c = 14.149$ (5) Å. The structure consists of a two-dimensional close-packed arrangement of $\text{Ti}(\text{urea})_6^{3+}$ units in columns parallel to the c axis. In the columnar interstices the perchlorate ions are arranged in spiral fashion. The structure is loosely linked by an extensive net of H bonds and van der Waals contacts and is closely analogous to that of the iodide salt (Davis & Wood, 1970). The geometry of the $\text{Ti}(\text{urea})_6^{3+}$ ion is formally octahedral with a superimposed trigonal distortion consisting of a twist about the threefold axis. Partial occupancy of two different sites is found for two of the four perchlorate oxygen atoms, but the geometry of the perchlorate ion remains essentially tetrahedral.

Introduction

During magnetic studies of transition metal coordination compounds it became desirable to investigate the properties of the Ti^{3+} (d^1) ion in a highly symmetrical environment, of close to regular octahedral stereochemistry. Accordingly, the hexaurea complex $\text{Ti}(\text{urea})_6(\text{ClO}_4)_3$ was selected as a suitable system in which to determine and correlate magnetic properties and structure. Independent work on the corresponding iodide salt became available after our structure was established (Linek, Siskova & Jensovsky, 1966; Linek, 1968; Davis & Wood, 1970) and it confirmed the structural details of the $\text{Ti}(\text{urea})_6^{3+}$ ion. Fowles, Lester & Wood (1969) have also described Ti^{3+} in octahedral coordination in $(\text{TiBr}_3)_2 \cdot 3\text{C}_4\text{H}_{10}\text{O}_2$.

Experimental preliminaries

In solution, the compound under study quickly oxidizes in air, so preparations were carried out in an atmosphere of nitrogen. The method, adapted from Barbieri (1915), is described by Wadley (1970). Microanalyses for carbon, hydrogen, and nitrogen, and analysis of titanium confirmed the purity of the product. (Found:

C, 10.34; H, 3.47; N, 23.56; Ti, 6.65%; required for $\text{Ti}(\text{urea})_6(\text{ClO}_4)_3$: C, 10.20; H, 3.42; N, 23.45; Ti, 6.78%.)

The crystals were deep blue, elongated hexagonal prisms of sizes ranging up to 3 mm diameter and 10 mm long. Many were simply hollow shells, with spaces almost from one end of the crystal to the other. The crystals, when dry, were quite stable to the atmosphere.

As expected, the temperature dependence of the paramagnetic susceptibility is in accord with an octahedrally coordinated titanium atom (Wadley, 1970). The titanium atom may be bonded with the six urea ligands *via* either the oxygen or nitrogen atom, although oxygen may be favoured by analogy with $\text{Ti}(\text{H}_2\text{O})_6^{3+}$ and from infrared assignments (Cotton & Wilkinson, 1962; Nakamoto, 1963). Many urea complexes are known to form a continuous urea framework with counter ions distributed in channels or voids of a suitable size, and a model consistent with this distribution may be favoured.

Crystals for X-ray data collection, about 0.2 mm diameter and 0.3 mm long, were cut from solid elongated prisms and examined under a polarizing microscope for cracks or other imperfections. After 60–70 hours of irradiation in the X-ray beam, the crystals

began to lose their intense blue colour, and eventually decomposed to a white powder. Since about 50 hours exposure time was required to record a single layer, it was necessary to use a different crystal for each layer. A coating of an aerosol lacquer was applied to protect the crystal from the atmosphere during irradiation.

The probable space group and approximate cell dimensions were obtained from Weissenberg and oscillation photographs using Ni-filtered Cu $K\alpha$ radiation. Cell dimensions were refined by least-squares methods, using data obtained from a Guinier camera employing Cu $K\alpha_1$ radiation with thoria ($a_0 = 5.5969 \text{ \AA}$) as internal standard. Crystal data are summarized in Table 1.

Table 1. Crystal data for $\text{Ti}(\text{urea})_6(\text{ClO}_4)_3$

$\text{C}_6\text{H}_{24}\text{N}_{12}\text{O}_{18}\text{Cl}_3\text{Ti}$	F.W.706.6
Lattice type:	rhombohedral
Cell dimensions (hexagonal cell):	$a_0 = 18.132 \pm 0.005 \text{ \AA}$
	$c_0 = 14.149 \pm 0.005$
	$Z = 6$
	$F(000) = 2166$
	$d_o = 1.73 \text{ g.cm}^{-3}$
	$d_c = 1.75 \text{ g.cm}^{-3}$
Observed reflexions:	$hkl: -h+k+l=3n$
	$hh0l: l=2n$
Space group:	$R\bar{3}c$; No. 167

Observed reflexions are consistent with the centrosymmetric space group $R\bar{3}c$ or its noncentrosymmetric subgroup $R3c$. The centrosymmetric space group was chosen for the initial structure determination, since it accommodates the unit-cell contents in a rational way and reduces the number of variable parameters considerably. This choice was confirmed by the satisfactory refinement.

Structure determination

Intensity data were collected using Zr-filtered Mo radiation and packs of three films of different speeds. The equi-inclination Weissenberg technique was used for layers $\langle hk0 \rangle$ to $\langle h, k, 11 \rangle$, while layers $\langle 0kl \rangle$, $\langle h0l \rangle$ and $\langle hhl \rangle$ ($l = -3 \dots 0 \dots +3$) were recorded on a precession camera.

Weissenberg intensities were determined visually by comparison with a standard series of spots whose lin-

earity was verified using a Joyce-Loebel microdensitometer. The densitometer was used directly to measure intensities on the precession films. The total number of independent reflexions used was 642. Unobserved

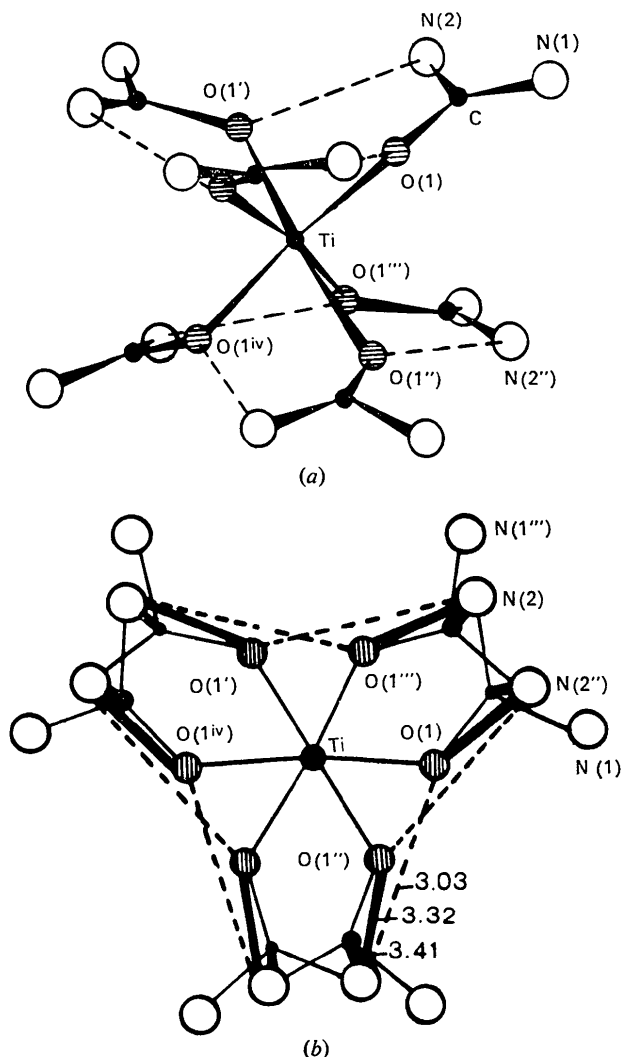


Fig. 1. Titanium urea cation. Possible H bonds are shown as broken lines. (a) General view of cation, (b) plan of cation showing fit of upper and lower halves. Van der Waals contacts are shown as heavy solid lines.

Table 2. Final positional parameters for $\text{Ti}(\text{urea})_6(\text{ClO}_4)_3$

Atom-position occupancy		$R = 0.122$			
		Values in parentheses are e.s.d.'s.			
		x	y	z	
C	36(f)	1.0	0.1587 (9)	0.0342 (9)	0.1361 (11)
O(1)	36(f)	1.0	0.1053 (5)	0.0565 (6)	0.1663 (7)
O(2)	36(f)	1.0	0.3527 (8)	0.0566 (8)	0.3023 (11)
O(3)	36(f)	0.5	0.4119 (25)	0.0577 (21)	0.1656 (28)
O(4)	36(f)	0.5	0.4447 (13)	0.0311 (22)	0.2158 (29)
N(1)	36(f)	1.0	0.2369 (7)	0.0956 (7)	0.1141 (10)
N(2)	36(f)	1.0	0.1365 (8)	-0.0449 (9)	0.1241 (11)
Ti	6(a)	1.0	0.0000 (0)	0.0000 (0)	0.2500 (0)
Cl	18(e)	1.0	0.3687 (3)	0.0000 (0)	0.2500 (0)

map indicated possible sites O(3) and O(4), separated by about 1 Å. Refinement left both sites equally occupied, with a total occupancy of unity. The residual was significantly better at 0.122, and reasonable interatomic distances were observed. Refinement was terminated when the shifts were less than about 0.1 of the estimated standard deviations. The parameters obtained in the last round of refinement are shown in Table 2, and 75 positional, thermal and scale factors were varied. Observed and calculated structure factors are given in Table 3. When unobserved reflexions were included at half the minimum observable value, the *R* value became 0.154. There was no significant change in parameters, but the e.s.d.'s decreased somewhat.

Thermal parameters are given in Table 4 to indicate their overall consistency and to show that no unreasonable anisotropy is suggested, except possibly for O(4). It is clear that the disordered oxygen atoms have higher thermal parameters and positional standard deviations than the other atoms, but the standard deviations are still an order of magnitude lower than the separation of the two sites. Bond lengths and angles are all reasonable (Table 5).

The difference Fourier map confirmed the model for the disordered perchlorate; it was without anomalies except in the special position 6(*a*), where a positive residual could be distinguished. This site is an ideal size to contain an oxygen atom, and two cycles of least-squares refinement were run assuming it to be partially occupied by a water molecule, which could have been incorporated during crystallization. The occupancy was found to be very low, of the order of 5%. Data are not sufficiently accurate to detect the hydrogen atoms of the urea molecule.

Description and discussion of the structure

The structure is composed of positively charged Ti(urea)_6^{3+} units, linked by hydrogen bonding to the negatively charged perchlorate ions. Intramolecular* bonding is partly by van der Waals contacts between the urea molecules and partly through a sharing of

each anion by four different Ti(urea)_6^{3+} groups as in the iodide salt. The simplest description of the structure involves (1) the geometry of the Ti(urea)_6^{3+} ions, (2) the perchlorate ion, and (3) the way in which these units pack together.

Titanium-urea complex

The six urea ligand molecules are coordinated to the central titanium atom *via* the oxygen atom O(1). The resulting unit is disc shaped and is stabilized by intramolecular hydrogen bonds N(2)–O(1) of 3.03 Å. These link each urea ligand molecule in the upper and lower parts to its two neighbours on the same level, forming saucer shaped ends to the disc (Fig. 1). Bonding between the upper and lower urea discs is by van der Waals contacts between N(2) and both carbon and oxygen atoms of the overlying urea.

The urea ligand molecule is planar, no atom being more than 0.01 Å from the plane determined by a least-squares fit. Also, it is almost coplanar with the intramolecular hydrogen bond. This may be the cause of the

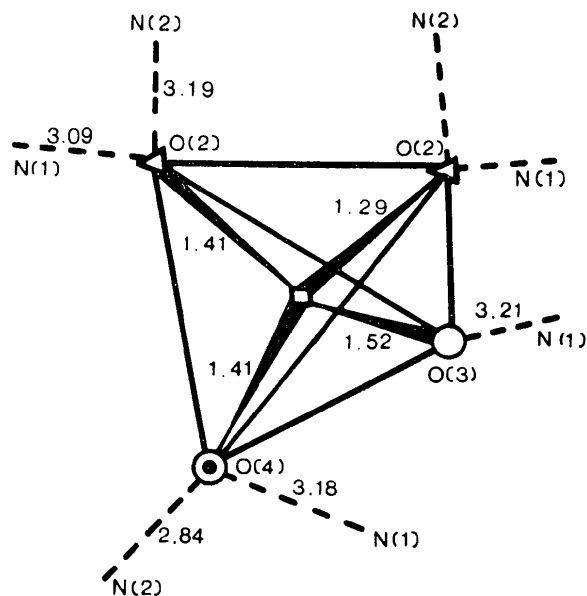


Fig. 2. One configuration of the perchlorate tetrahedron showing bond lengths and shortest contacts with urea ligands.

* For the purposes of this discussion, bonds within the Ti(urea)_6 unit will be called intramolecular, and bonds between the units intermolecular.

Table 4. Anisotropic temperature factors for $\text{Ti(urea)}_6(\text{ClO}_4)_3$

$$\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} - 2kl\beta_{23})]$$

Numbers in parentheses are e.s.d.'s.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C	0.0038 (6)	0.0040 (6)	0.0033 (9)	0.0021 (5)	-0.0002 (6)	-0.0012 (6)
O(1)	0.0031 (4)	0.0034 (4)	0.0046 (6)	0.0021 (4)	0.0012 (4)	0.0006 (4)
O(2)	0.0066 (7)	0.0048 (5)	0.0094 (11)	0.0032 (5)	0.0003 (7)	-0.0023 (7)
O(3)	0.0100 (23)	0.0067 (16)	0.0120 (32)	0.0049 (17)	0.0002 (23)	0.0024 (18)
O(4)	0.0012 (9)	0.0104 (31)	0.0180 (52)	-0.0004 (10)	0.0031 (16)	-0.0035 (27)
N(1)	0.0026 (5)	0.0035 (5)	0.0071 (9)	0.0009 (4)	0.0014 (6)	0.0001 (6)
N(2)	0.0045 (7)	0.0052 (7)	0.0075 (11)	0.0027 (6)	0.0018 (7)	0.0028 (7)
Ti	0.0017 (1)	0.0017 (1)	0.0023 (3)	0.0008 (1)	0.0000 (0)	0.0000 (0)
Cl	0.0040 (1)	0.0040 (1)	0.0047 (3)	0.0020 (1)	0.0000 (0)	0.0000 (0)

paddle-like tilt of the urea molecules. Bond distances and angles for the urea molecule in Table 5 are similar to distances in a great many urea complexes, including the isomorphous compound $\text{Ti(urea)}_6\text{I}_3$ (Linek, 1968, Davis & Wood, 1970).

Oxygen atoms around the titanium atom form a trigonally distorted octahedron. All titanium–oxygen distances are equal at 2.04 Å, compared to 2.01 Å quoted by Davis & Wood (1970) for the iodide salt. As they point out, the distortion consists of a rotation of the upper triangular face with respect to the lower face by about 5°, and occurs without compression or relaxation along the trigonal axis. It is not possible to assess whether this distortion is due to the Jahn–Teller effect, or to the adoption of a geometry that maximizes van der Waals bonding and minimizes steric interference. The interaction of the urea carbon, oxygen, and N(2) atoms [projection in Fig. 1(b)] strongly suggests that van der Waals bonding between the overlying urea molecules is important, while the similarity of the distortion in the iodide salt makes hydrogen bonding a less likely cause.

The perchlorate ion

The structure and disorder of the perchlorate ion are of great interest. A search of the literature for details of X-ray structural determinations involving perchlorate ions showed some confusion on the subject. Cotton & Weaver (1965), for example, report the structure of a cobalt t(II) compound, in which the perchlorate anion shows chlorine–oxygen distances of 1.41–1.47 Å and angles of 104–113°. Many other perchlorate structures reported in the literature indicate a closely tetrahedral arrangement. However, Karle &

Karle (1966) describe an ordered perchlorate anion with a range of bond lengths from 1.36 to 1.46 Å and angles from 96.3–117.4°; Blundell & Powell (1967) found very large thermal parameters, bond lengths of 1.36–1.42 Å, and bond angles of 99–117° for the perchlorate ion in a palladium complex compound. Pauling, Robertson & Rodley (1965) and Einstein & Rodley (1967) reported difficulty in locating the oxygen atoms in two perchlorate complexes because of a high degree of disorder.

In our case, the disorder involves only two of the four perchlorate oxygen atoms. It cannot be satisfactorily resolved using a four-oxygen-atom-model, but requires one pair of oxygen atoms to be split into two pairs of half-occupied sites, separated by a distance of only 1.17 Å. Because of this short distance, the disordered sites cannot be occupied at random. The position of the chlorine atom is independent of the pair of oxygen sites that is occupied, and the atom has nearly isotropic thermal vibration. The perchlorate ion geometry is still close to tetrahedral (Fig. 2 and Table 5). The asymmetry seems to be due to the fact that occupancy of the O(4) sites enables the formation of a very strong hydrogen bond (2.84 Å) with the atom N(2), while the alternative O(3) site may also be bonded to the N(1) atom (3.21 Å). Fig. 2 also shows the shortest contact distances to the perchlorate ions. In the strictly tetrahedral position, both oxygen atoms could be involved in medium strength H bonds of length about 3.1 Å. The ‘good’ oxygen atoms [O(2)] are well situated with respect to N(1) and N(2) to form H bonds of lengths 3.09 and 3.19 Å, respectively.

Apparently, individual unit cells do not fulfil the requirements of space group $R\bar{3}c$, but the average statis-

Table 5. Bond lengths and angles for $\text{Ti(urea)}_6(\text{ClO}_4)_3$

Ti (urea) ₆ ³⁺ unit		Perchlorate ion (prime indicates atom at $x-y, \bar{y}, \frac{1}{2}-z$)	
Ti—O(1)	2.04 (1) Å	Cl—O(2)	1.41 (1) Å × 2
O(1)—C	1.29 (1)	Cl—O(3)	1.52 (3)
C—N(1)	1.33 (2)	Cl—O(4)	1.29 (2)
C—N(2)	1.29 (2)	O(2)—O(2')	2.31 (2)
O(1)—O(1')	2.87 (1)	Other O—O distances from 2.14 to 2.36 Å	
O(1)—O(1'')	2.96 (2)	O(2)—Cl—O(2')	110.3 (11)°
O(1)—O(1''')	2.82 (2)	O(2)—Cl—O(3')	93.5 (16)
N(2)—N(2''')	3.83 (2)	O(2)—Cl—O(4)	116.2 (15)
N(1)—N(2''')	3.83 (2)	O(2')—Cl—O(3')	97.7 (14)
O(1)—N(2''')	3.32 (2)	O(2')—Cl—O(4)	121.7 (16)
C—N(2''')	3.41 (2)	O(3')—Cl—O(4)	112.0 (25)
N(2)—H...O(1')	3.03 (2)		
Between units			
O(1)—Ti—O(1')	89.6 (4)°	(i) Faces N(1)—N(2)	3.70 (2) Å
O(1)—Ti—O(1'')	87.8 (5)	(ii) Edges N(1)—N(1')	3.47 (2)
O(1)—Ti—O(1''')	176.1 (5)		
O(1)—Ti—O(1''')	93.3 (5)		
Ti—O(1)—C	134.0 (9)	To perchlorate ion	
O(1)—C—N(1)	117.9 (12)	N(2)—O(4)	2.84 (4) × $\frac{1}{2}$
O(1)—C—N(2)	121.5 (13)	N(1)—O(2)	3.09 (2)
N(1)—C—N(2)	120.6 (13)	N(2)—O(2)	3.19 (2)
		N(1)—O(3)	3.21 (4) × $\frac{1}{2}$
		N(1)—O(4)	3.18 (4) × $\frac{1}{2}$
		Other perchlorate contacts of 3.31 and 3.37 Å	

(See Fig. 1. for key to transformations).

tical structure does fulfil these requirements. The fact that the occupancy of the disordered sites is close to half suggests that the disorder is a real effect. A very similar type of disorder was reported recently by Ozbirn & Jacobson (1970) whose model for the perchlorate ion parallels ours.

Packing considerations

The structure of $\text{Ti(urea)}_6(\text{ClO}_4)_3$ as a whole resembles many urea complexes and adducts, in that the general framework is due largely to packing characteristics of the urea molecules and the anions are distributed interstitially. The Ti(urea)_6^{3+} units are stacked one above the other, every second unit being inverted with respect to the first. The resulting, almost circular, columns are close-packed in two dimensions. Each Ti(urea)_6^{3+} unit may be approximated by a cylinder 7.1 Å high and 10.5 Å in diameter. The actual N–N distance between the edges of the discs is 3.47 Å, a normal van der Waals diameter (Bondi, 1968). The N–N contacts between the faces of the discs, on the other hand, are very long (3.70 Å) and approximate the similar contacts within each unit (3.83 Å). Evidently, closest distances of approach to the N_2H_4 subunit of the urea molecule vary with direction, being least for contacts parallel to the urea plane and most for contacts perpendicular to this plane. A similar situation occurs in thiourea, which contains N–N contacts of 3.85 Å perpendicular to the thiourea plane (Wyckoff, 1966).

In the triangular channels between the columns of urea molecules the perchlorate ions fit loosely. By forming a threefold spiral in which the perchlorate ions are displaced towards the corners of the triangles, they are accommodated snugly and tend to bind two columns together, as well as linking discs within the columns. Thus, besides the van der Waals bonding between nitrogen atoms and the ionic bonding to the interstitial perchlorate ions, H bonding from the perchlorate oxygen atoms to nitrogen atoms of the adjacent urea molecules helps to stabilize the structure as in the iodide. The N–O contacts are listed in Table 5.

The structure at low temperature, now under investigation, may also throw some light on these problems. This, together with the structure of the isomorphous

vanadium urea iodide, will form the basis of later papers in this series.

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