

The Structure of Ammonium Pertechnetate at 295, 208 and 141 K

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Abstract

$\text{NH}_4[\text{TcO}_4]$, tetragonal, $I4_1/a$, $a = 5.775(2)$, $c = 13.252(5)$ Å, $U = 442.0$ Å³, $Z = 4$, $M_r = 180.94$, $D_x = 2.72$, $D_{\text{obs}} = 2.72(2)$ Mg m⁻³ at 295 K. $R = 0.0166$, $R_w = 0.0226$ based on 304 diffractometer-measured reflections. The structure comprises discrete ammonium and pertechnetate ions, held together by hydrogen bonding. Bond distances are normal. Structural determinations at 208 and 141 K showed only small differences caused by rotation of the NH_4^+ and $[\text{TcO}_4]^-$ ions about the fourfold axis and some angular distortion of the ammonium ion at 208 K.

Introduction

Ammonium pertechnetate has been studied extensively by nuclear quadrupole resonance and X-ray crystallography (Brown, Smeltzer & Heyding, 1976, and references therein; Faggiani, Lock & Soderholm, 1977; Reynhardt & Kruger, 1978), because it shows anomalous temperature dependence of the NQR frequency. Further, ammonium perrhenate 'exhibits anomalous temperature coefficients which are large and positive along the c axis, and large and negative along the a axis' (Brown *et al.*, 1976). Single-crystal structure studies have shown no trace of the H atoms at 295 K, but they could be detected at 135 K (Reynhardt & Kruger, 1978). It was of interest to see whether similar structural effects could be seen for ammonium pertechnetate.

Experiments

Crystals were prepared by slow evaporation of a solution of $\text{NH}_4[\text{TcO}_4]$ loaned to us by the McMaster University Health Physics Group. The crystals separated as tetragonal bipyramids. Two crystals were selected for experiments. One was used for structure determination at 295 and 141 K, the other at 208 K.

Precession photographs confirmed the systematic absences for $I4_1/a$ at each temperature. The first crystal was used to gather a series of cell parameters as

a function of temperature (except for the point at 208 K, which was obtained from the second crystal) using a least-squares fit of 15 well centered reflections ($11.6 < 2\theta < 42.5^\circ$) on a Syntex $P2_1$ diffractometer. The density at room temperature was determined by flotation in a diiodomethane–iodoethane mixture yielding $Z = 4$ for the title formula. Intensities were measured to $2\theta = 55^\circ$ with Mo $K\alpha$ radiation. The computer-controlled Syntex $P2_1$ diffractometer was operated in a $\theta(\text{crystal})-2\theta(\text{counter})$ scan mode. Data which varied from crystal to crystal are summarized in Table 1. The method of data treatment has been described previously (Hughes, Krishnamachari, Lock, Powell & Turner, 1977; Lippert, Lock, Rosenberg & Zvagulis, 1977). The crystals were chosen to be sufficiently small so that no correction was needed for absorption: the maximum error in F was 1%. Corrections were made for secondary extinction (Larson, 1967).

O atoms were located from a difference map and the atom positions and anisotropic temperature factors were refined using full-matrix least squares, minimizing $\sum w(|F_o| - |F_c|)^2$. When refinement was stopped a difference synthesis revealed the H atoms. The H positional parameters and subsequently the temperature factor were added to the variables in the refinement, statistical tests (Hamilton, 1965) showing

Table 1. *Crystal data*

Temperature (K)	295	208	141
Crystal size (mm)	0.05 × 0.03 × 0.03	0.045 × 0.03 × 0.03	0.05 × 0.03 × 0.03
μ (mm ⁻¹)	0.308	0.312	0.315
a (Å)	5.775 (2)	5.769 (2)	5.741 (2)
c (Å)	13.252 (5)	13.090 (5)	13.121 (7)
Number of independent reflections	304	294	299
Number with $I > 3\sigma(I)$	267	261	272
Final R^*	0.0166	0.0264	0.0142
Final R_w^*	0.0226	0.0313	0.0184
Final shift in e.s.d.			
maximum	0.148	0.075	0.049
average	0.031	0.026	0.012
Weighting scheme	$1/w = (1.2377 - 0.0424 F_o + 0.000798 F_o ^2)$	$1/w = (1.1160 - 0.0653 F_o + 0.00182 F_o ^2)$	$1/w = (1.7604 - 0.0416 F_o + 0.000764 F_o ^2)$

$$* R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, R_w = \left[\frac{\sum w(|F_o| - |F_c|)^2}{\sum wF_o^2} \right]^{1/2}$$

the additional parameters were justified. Refinement was terminated when the maximum shift/error was less than 0.15. Scattering factors were taken from Cromer & Waber (1974) and a correction for anomalous scattering was applied to Tc (Cromer, 1974). Final difference maps were essentially featureless with no peaks over $0.6 \text{ e } \text{Å}^{-3}$ or valleys less than $-0.5 \text{ e } \text{Å}^{-3}$. Atom parameters and isotropic temperature factors are given in Table 2.*

Raman spectra were recorded on a Spex Industries Model 1400 0.75 m Czerny–Turner double monochromator using a Spectra Physics Model 164 argon ion laser operating at 1000 mW at 5145 Å.

* Lists of structure factors and anisotropic thermal parameters obtained at 295, 208 and 141 K, and the cell constants, volume and axial ratio as a function of temperature have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34821 (6 pp.) Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Atom parameters for $\text{NH}_4[\text{TcO}_4]$ at 295, 208, and 141 K

		295 K	208 K	141 K
Tc	$U_{\text{eq}} (\text{Å}^2)$	0.0228 (4)	0.0132 (6)	0.0081 (2)
N	$U_{\text{eq}} (\text{Å}^2)$	0.028 (3)	0.016 (3)	0.009 (2)
O	x	0.0991 (4)	0.1087 (4)	0.1107 (3)
	y	0.4706 (4)	0.4673 (4)	0.4676 (3)
	z	0.1985 (2)	0.1996 (2)	0.1998 (1)
	$U_{\text{eq}} (\text{Å}^2)$	0.046 (1)	0.025 (1)	0.0173 (7)
H	x	0.109 (9)	0.081 (10)	0.097 (6)
	y	0.224 (13)	0.211 (8)	0.189 (7)
	z	0.593 (3)	0.580 (4)	0.593 (2)
	$U_{\text{iso}} (\text{Å}^2)$	0.24 (2)	0.19 (2)	0.18 (1)

Tc was at the special position $0, \frac{1}{4}, \frac{1}{8}$ and N at the special position $0, \frac{1}{4}, \frac{3}{8}$ based on a cell with the origin at $\bar{1}$ at $0, \frac{1}{4}, \frac{3}{8}$ from 4. $U_{\text{eq}} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.

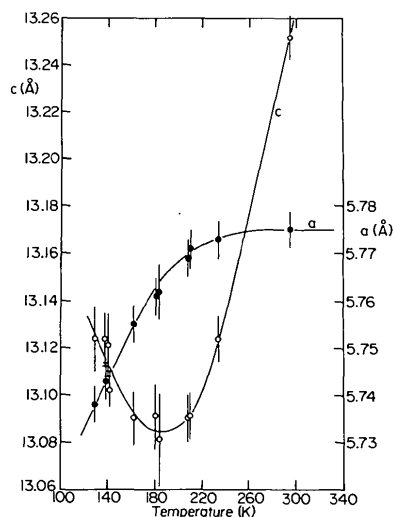


Fig. 1. Variation of the cell parameters of $\text{NH}_4[\text{TcO}_4]$ with temperature (2σ limits).

Results and discussion

The variation of the cell constants of $\text{NH}_4[\text{TcO}_4]$ with temperature is given in Fig. 1. There is a resemblance to the behavior of $\text{NH}_4[\text{ReO}_4]$ (Brown *et al.*, 1976) only at low temperature (129–180 K) where the c value is falling and a rising. After 180 K the trend reverses and c increases. At about the same temperature there is a change in the slope of the a increase which continues to rise much more slowly. These changes have very little effect on the volume of the cell, which increases smoothly over the temperature range 129–295 K (Fig. 2). The effect is dramatized, however, by plotting the axial ratio c/a against temperature (Fig. 2) where a minimum appears at about 210 K. This might indicate a phase transition, but, as we shall show later, there is relatively little change in structure above and below the minimum. There is another significant difference from $\text{NH}_4[\text{ReO}_4]$, and this is that the cell volume for $\text{NH}_4[\text{TcO}_4]$ is larger than that for $\text{NH}_4[\text{ReO}_4]$ throughout the whole temperature range, which is surprising since the Tc–O distances [1.702 (2)–1.711 (1) Å] are smaller than the corresponding Re–O distances [1.737 (7), 1.720 (5) Å]. Because of the changes in the axial ratio we determined the crystal structure of $\text{NH}_4[\text{TcO}_4]$ at 295, 208, and 141 K. It proved possible to locate all atoms, although the H atoms have large temperature factors. Despite the changes in the cell parameters the variation in structure with temperature is not remarkable (see Table 3). At 208 K the NH_4^+ is significantly distorted from tetrahedral symmetry, even though the errors are large, whereas it is not at 295 and 141 K. This does not, however, change the hydrogen-bonding pattern significantly and there is a fairly steady decrease in non-bonding O–N and O–O distances with temperature.

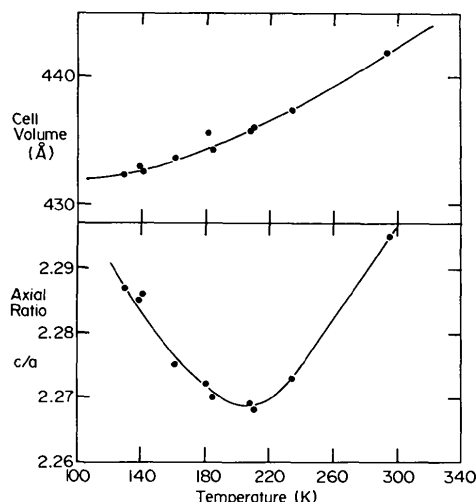


Fig. 2. Variation of the cell volume and the axial ratio c/a of $\text{NH}_4[\text{TcO}_4]$ with temperature.

Table 3. Selected interatomic distances (Å) and angles (°)

	298 K	208 K	141 K
Tc—O	1.702 (2)	1.709 (2)	1.711 (1)
N—H	0.77 (6)	0.78 (5)	0.78 (3)
O—H ^(a)	2.27 (5)	2.23 (5)	2.24 (4)
O—H ^(b)	2.44 (5)	2.38 (5)	2.37 (3)
O—O ^(f)	3.194 (3)	3.172 (3)	3.158 (2)
N—O ^(g)	2.899 (2)	2.885 (2)	2.883 (1)
N—O ^(h)	2.984 (2)	2.951 (2)	2.930 (2)
O—Tc—O ^(c)	110.2 (1)	110.3 (1)	110.0 (1)
O—Tc—O ^(d)	109.1 (1)	109.1 (1)	109.2 (1)
H—N—H ^(e)	114 (6)	125 (5)	115 (3)
H—N—H ^(e)	107 (6)	82 (5)	107 (3)
N—H—O ^(g)	139 (6)	142 (6)	148 (3)
N—H—O ^(h)	129 (6)	131 (6)	124 (3)

Superscripted atoms are related to those given in Table 2 by the following transformations: (a) $y - \frac{1}{4}, \frac{3}{4} - x, z - \frac{1}{2}$; (b) $\frac{1}{4} + y, \frac{3}{4} - x, \frac{3}{4} - z$; (c) $-x, \frac{1}{2} - y, z$; (d) $\frac{1}{4} - y, \frac{1}{4} + x, \frac{1}{4} - z$; (e) $\frac{1}{4} - y, \frac{1}{4} + x, 1\frac{1}{4} - z$; (f) $\frac{1}{2} + x, y, \frac{1}{2} - z$; (g) $\frac{1}{4} - y, \frac{1}{4} + x, \frac{1}{4} + z$; (h) $y - \frac{3}{4}, \frac{3}{4} - x, \frac{3}{4} - z$.

The O—H hydrogen-bonding distances, however, stay essentially constant. These changes may be associated with a small rotation of the NH_4^+ and $[\text{TcO}_4]^-$ ions which takes place about the fourfold axis as the temperature is lowered. Both rotations take place in the same sense: the NH_4^+ ion rotates 12.3 and 6.4° and the $[\text{TcO}_4]^-$ ion 2.4 and 0.4° between $295 \rightarrow 208$ K and $208 \rightarrow 141$ K. Surprisingly the Tc—O distance apparently increases with lowered temperature.

The Raman spectrum of a powdered sample of $\text{NH}_4[\text{TcO}_4]$ was recorded over a range of temperatures, but it, also, showed little change. The only evidence of absorptions caused by the NH_4^+ ion was a very weak broad absorption between 3100 and 3200 cm^{-1} which showed no detail. Absorptions below 1000 cm^{-1} , which arise from the $[\text{TcO}_4]^-$ ion and lattice modes, were much better resolved. These showed little variation with temperature and are summarized in Table 4. The only significant change was that the broad weak peak at ~ 100 cm^{-1} could be resolved into two broad peaks below 243 K.

Table 4. Raman spectrum of powdered $\text{NH}_4[\text{TcO}_4]$ (based on spectra at 295, 243, 223, 213, 203 and 183 K)

Line wave number (cm^{-1})	Intensity (908 $\text{cm}^{-1} = 100$)	Assignment (based on T_d symmetry)	
38 (2)*	1.3 (0.2)	} lattice modes?	
58 (1)	18 (2)		
77 (1)	0.6 (0.2)		
92 (2)	2 (0.5)		
102 (2)	2.5 (0.5)		
116 (2)	0.3 (0.1)		
326 (1)	32 (2)		$\nu_2 (e)$
341 (2)	5 (0.5)		$\nu_4 (t_2)$
352 (1)	8 (1)		
880 (2)	35 (3)		$\nu_3 (t_2)$
908 (2)	100 (6)	$\nu_1 (a_1)$	

* Values in parentheses show variation limits for the six spectra.

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