

Raman spectroscopy of silver
pertechnetateMark J. Sarsfield,^{a*} Andrew D. Sutton,^a Francis R. Livens,^a
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The title compound, AgTcO₄, contains close Ag—O contacts, and Raman spectroscopy shows a reduction in the Tc—O stretching frequencies on changing the pertechnetate counter-cation from K⁺ to Ag⁺.

Comment

Within the nuclear industry, technetium is an important fission product that exists predominantly in the highest oxidation state, *i.e.* Tc^{VII}, as the pertechnetate anion [TcO₄][−]. An understanding of the chemistry of pertechnetate in forming complexes, either through covalent bonding or as a counter-anion, is important in the context of nuclear fuel reprocessing and waste management (Wilson, 1996). It has been shown previously that the perrhenate analogue, [ReO₄][−], readily forms complexes through oxygen coordination to a range of *d* and *f* transition metal centres (Chakravorti, 1990). However, there have been no related investigations into the coordinating ability of [TcO₄][−], possibly because all Tc isotopes are radioactive. We describe here evidence that, in the solid state, considerable covalent-bonding interactions occur between pertechnetate anions and silver cations.

The compound AgTcO₄ crystallizes in a high-symmetry space group (*I*4₁/*a*), with three atoms in the asymmetric unit, and is isostructural with AgReO₄ (Naumov *et al.*, 1999). A packing diagram and a polyhedral representation of the bonding around the Tc and Ag atoms are shown in Fig. 1. Interatomic distances and angles are shown in Table 1. The 16th, 17th and 18th lowest O—Ag—O bond angles are equivalent, predicting a triangular dodecahedral geometry around the Ag atom (Fig. 1*b*) according to the coordination geometry rules for eight-coordinated complexes (Haigh, 1995). The Tc atom resides in a slightly distorted tetrahedron in AgTcO₄, with O—Tc—O angles of 108.52 (16) and 111.4 (3)°, compared with 110.0 (1)° and 109.2 (1)° in (NH₄)[TcO₄] and 110.5 (2)° and 109.0 (2)° in KTcO₄. Each O atom bridges one Tc and two Ag atoms. The Tc—O bond

length [1.724 (5) Å] is similar to that in KTcO₄ [1.711 (3) Å; Krebs & Hasse, 1976], (NH₄)[TcO₄] [1.711 (1) Å; Faggiani *et al.*, 1980] and AgReO₄ [Re—O = 1.732 (4) Å; Naumov *et al.*, 1999]. The average Ag—O bond lengths in AgTcO₄ [2.532 (5) and 2.596 (5) Å, mean 2.564 Å] are shorter than those in the isostructural compound AgClO₄ [2.728 (6) and 2.527 (6) Å, mean 2.627 Å; Berthold *et al.*, 1976] and are considerably shorter than those in KTcO₄ [2.794 (3) and 2.864 (3) Å, mean 2.829 Å; Krebs & Hasse, 1976], even after correction for the difference in ionic radii (mean 2.699 Å; *r*K⁺ − *r*Ag⁺ = 0.13 Å for eight-coordinated *M*⁺ ions; Winter, 2002).

The short Ag—O contact in AgTcO₄ suggests an unusually strong interaction between the pertechnetate and silver ions, which can be detected by the influence on the Tc—O bond strengths. When considering the relative bond strengths in related compounds, the difference in stretching frequency ($\Delta\nu$) in Raman spectroscopy is more sensitive as a probe than X-ray diffraction techniques. In order to interpret the Raman spectrum of AgTcO₄ we have collated Raman data for the related compounds KTcO₄, (NH₄)[TcO₄], AgReO₄ and KReO₄ (Table 2); all contain the [MO₄][−] ion with the same *S*4 site symmetry, allowing a comparative study (Wilson *et al.*, 1955; Decius & Hexter, 1977). The correlation tables for such site symmetry predict three Raman-active stretching vibration frequencies, *viz.* one symmetric vibration [*A* species, $\nu_1(a_1)$], which is identified by polarization experiments, and two asymmetric vibrations assigned to *B* and *E* [both from $\nu_3(f_2)$], with *E* being of higher intensity than *B* (Wilson *et al.*, 1955). Raman data for KTcO₄ (Busey & Keller, 1964), a compound with long K—O bond lengths (see above) and weak cation–oxygen interactions, has slightly higher symmetric and asymmetric vibrations (Table 2) than those observed for (NH₄)[TcO₄] [$\Delta\nu_1 = 5$, $\Delta\nu_3(B) = 12$ and $\Delta\nu_3(E) = 7$ cm^{−1}; Faggiani *et al.*, 1980] because of the hydrogen-bonding network within the structure of the latter. By comparison,

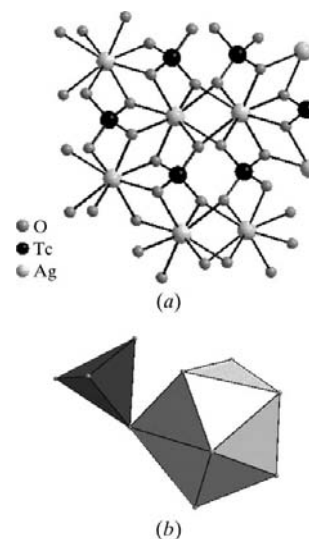


Figure 1
(*a*) The extended lattice of AgTcO₄, viewed along the crystallographic *b* axis. (*b*) A polyhedral representation of the geometry around the Ag and Tc atoms.

stretching vibrations for AgTcO_4 are shifted to a much lower energy relative to KTcO_4 [$\Delta\nu_1 = 33$, $\Delta\nu_3(B) = 24$ and $\Delta\nu_3(E) = 40 \text{ cm}^{-1}$], and such large shifts in the Raman lines infer considerable covalent bonding between silver and pertechnetate ions in the solid state. Substantial Raman shifts to lower frequency are common for related AgMO_4 compounds when compared with their respective potassium salts (Hester & Plane, 1964); indeed, there are large shifts to lower frequency in the Raman lines for perrhenate ions [$\Delta\nu_1 = 24$, $\Delta\nu_3(B) = 25$ and $\Delta\nu_3(E) = 35 \text{ cm}^{-1}$; Busey & Keller, 1964].

Both single-crystal X-ray diffraction and Raman spectroscopy indicate that there are significant interactions between Ag^+ and $[\text{TcO}_4]^-$ ions, suggesting that $[\text{TcO}_4]^-$ may be on a par with or better than perrhenate as a coordinating ligand to other metal centres.

Experimental

The title compound was synthesized as described by Nugent (1983). Recrystallization from water afforded pale-yellow crystals suitable for X-ray analysis.

Crystal data

AgTcO_4	Mo $K\alpha$ radiation
$M_r = 269.87$	Cell parameters from 779 reflections
Tetragonal, $I4_1/a$	$\theta = 6.5\text{--}28.1^\circ$
$a = 5.3026$ (12) Å	$\mu = 9.89 \text{ mm}^{-1}$
$c = 11.810$ (5) Å	$T = 100$ (2) K
$V = 332.07$ (18) Å ³	Block, yellow
$Z = 4$	$0.20 \times 0.10 \times 0.10 \text{ mm}$
$D_x = 5.398 \text{ Mg m}^{-3}$	

Data collection

Bruker CCD area-detector diffractometer	204 independent reflections
φ and ω scans	200 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan [SADABS (Sheldrick, 1996) and SHELXTL (Bruker, 1998)]	$R_{\text{int}} = 0.016$
$T_{\text{min}} = 0.242$, $T_{\text{max}} = 0.438$	$\theta_{\text{max}} = 28.1^\circ$
1395 measured reflections	$h = -7 \rightarrow 6$
	$k = -6 \rightarrow 6$
	$l = -15 \rightarrow 15$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0288P)^2 + 9.6708P]$
$R(F) = 0.039$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.093$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.45$	$\Delta\rho_{\text{max}} = 0.69 \text{ e \AA}^{-3}$
204 reflections	$\Delta\rho_{\text{min}} = -1.19 \text{ e \AA}^{-3}$
10 parameters	

The metal atoms were refined anisotropically and atom O1 was refined isotropically.

Data collection: SMART (Bruker, 1997); cell refinement: SMART; data reduction: SAINT (Bruker, 1997); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: DIAMOND (Brandenburg, 2001); software used to prepare material for publication: SHELXTL (Bruker, 1998).

Table 1

Selected geometric parameters (Å, °).

Ag1—O1^{i}	2.532 (5)	Tc1—O1	1.724 (5)
$\text{Ag1—O1}^{\text{ii}}$	2.596 (5)		
$\text{O1—Tc1—O1}^{\text{iii}}$	108.52 (16)	$\text{O1}^{\text{iii}}\text{—Tc1—O1}^{\text{iv}}$	111.4 (3)

Symmetry codes: (i) $\frac{3}{4} - y, \frac{1}{4} + x, \frac{1}{4} + z$; (ii) $y - \frac{1}{4}, \frac{1}{4} - x, \frac{1}{4} - z$; (iii) $y - \frac{1}{4}, \frac{5}{4} - x, \frac{1}{4} - z$; (iv) $\frac{5}{4} - y, \frac{1}{4} + x, \frac{1}{4} - z$.

Table 2

Raman lines (cm^{-1}) and assignments for pertechnetate and perrhenate compounds.

Compound	ν_1^\dagger	$\nu_3(E)^\dagger$	$\nu_3(B)^\dagger$
AgTcO_4^\ddagger	880 (v)	847 (m)	896 (w)
$[\text{NH}_4][\text{TcO}_4]^\S$	908 (v)	880 (m)	¶
KTcO_4^\ddagger	913 (v)	887 (m)	920 (w)
AgReO_4^\ddagger	942 (v)	862 (m)	899 (w)
KReO_4^\ddagger	966 (v)	897 (m)	924 (w)

† Relative intensity in parentheses; v is very strong, m is medium and w is weak. ‡ This work. § Faggiani *et al.* (1980). ¶ This signal lies beneath the 908 cm^{-1} signal (Faggiani *et al.*, 1980). †† Busey & Keller (1964). ‡‡ Otto *et al.* (1991).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1620). Services for accessing these data are described at the back of the journal.

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