

Inorganica Chimica Acta

LETTER

Nitridotechnetium(VI) aqueous solution chemistry

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(Received October 15, 1990)

We have recently reported the hydrolysis of $\text{Cs}_2[\text{TcNCl}_5]$ to give a brown precipitate of 'TcN(OH)₃' [1]. This compound was named nitridotechnetic(VI) acid (1) on the basis of its solubility in 1 M hydroxide solution and a supposed relationship to nitridoosmic(VIII) acid, $[\text{Os}(\text{N})\text{O}_3\text{H}]$ ('osmiumic acid'), and to the hypothetical nitridorhenic(VII) and nitridomolybdic(VI) acids which are known as the $\text{M}_2[\text{Re}(\text{N})\text{O}_3]$ and $\text{M}_3[\text{Mo}(\text{N})\text{O}_3]$ salts, respectively [2]. We now report properties of 1 and of $\text{Cs}_2[\text{TcNCl}_5]$ which show close parallels, and some significant differences, to those of the isoelectronic 'MoO(OH)₃' and $\text{M}_2[\text{MoOCl}_5]$.

Experimental

$\text{Cs}_2[\text{TcNCl}_5]$ was prepared by the methods described previously [3, 4] and $\text{MoO}(\text{OH})_3$ by the addition of NaOH to a solution of $(\text{NH}_4)_2[\text{MoOCl}_5]$ [5]. Infrared spectra were determined in KBr discs. ESR spectra were obtained by use of a Bruker ESR-200 D spectrometer.

$\text{Cs}_2[\text{Tc}_2\text{N}_2\text{O}_2(\text{OH})_4]$ (2)

Nitridotechnetic(VI) acid (1) prepared by the hydrolysis of $\text{Cs}_2[\text{TcNCl}_5]$ (130 mg, 0.234 mmol) was added to a solution of $\text{CsOH}\cdot\text{H}_2\text{O}$ (300 mg, 1.8 mmol) in 1.8 cm³ of water. The mixture was vigorously shaken and a further 3 cm³ of water added to give a slightly cloudy solution. Filtration through a 0.22 μm filter gave a yellow-brown solution which on addition of ethanol precipitated a yellow powder. The mixture was centrifuged and the precipitate

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twice resuspended in ethanol and recentrifuged to remove CsOH and any Cs_2CO_3 . Compound 2 was dried under vacuum. Yield 45 mg (65% based on $\text{Cs}_2[\text{TcNCl}_5]$). *Anal.* Calc. for $\text{Cs}_2\text{H}_4\text{N}_2\text{O}_6\text{Tc}_2$: H, 0.68; N, 4.73; Tc, 33.4. Found: H, 0.84; N, 4.73; Tc, 33.2%. The microanalysis also showed the presence of 0.35% C, indicating the retention of a trace of ethanol. On heating, 2 turned brown and then black but did not melt at up to 360 °C. The IR spectrum showed peaks at ~3600–2800(broad), 1628w, 1046vs, 734s and 639s cm⁻¹.

Reaction of 2 with HCl

12 mg (0.02 mmol) of 2 was dissolved in 1 cm³ of 6 M HCl to give an intense purple-blue solution which rapidly turned orange on gentle warming. Addition of AsPh_4Cl (20 mg in 0.4 cm³ of water) gave an orange precipitate of $\text{AsPh}_4[\text{TcNCl}_4]$ which was collected by filtration and washed with 6 M HCl. Yield 24.5 mg (95%).

$[\{\text{TcN}(\text{S}_2\text{CNET}_2)\}_2(\mu\text{-O})_2]$ (3)

$\text{Cs}_2[\text{TcNCl}_5]$ (70 mg, 0.126 mmol) was dissolved with shaking in 4 cm³ of 0.25 M NaOH to give a yellow-brown solution. On addition of $\text{Na}(\text{S}_2\text{CNET}_2)\cdot 3\text{H}_2\text{O}$ (85 mg, 0.38 mmol) in 1 cm³ of water the mixture became cloudy and a yellow precipitate formed. The mixture was extracted with CH_2Cl_2 (2 × 4 cm³) and the extract dried over anhydrous Na_2SO_4 . The extract was reduced in volume and applied to a silica gel (230–430 mesh) column and eluted with CH_2Cl_2 . The first yellow fraction of $[\text{TcN}(\text{S}_2\text{CNET}_2)_2]$ (3.0 mg, 6% yield) was followed by a well-separated yellow band of 3 (17.4 mg, 50% yield), m.p. decomposes at c. 213 °C. Absolute ethanol was added to solutions of 3 in CH_2Cl_2 prior to evaporation to dryness as this prevented the formation of a purple colouration.

Electrophoresis

Electrophoretic separations were performed on a CAMAG high voltage electrophoresis system using 2 × 44 cm Whatman no. 1 paper strips. The supporting electrolyte was a 0.5 M solution of toluene-*p*-sulfonic acid (Hpts), $\text{CF}_3\text{SO}_3\text{H}$, $\text{CH}_3\text{SO}_3\text{H}$ or KHSO_4 . The separations were performed at 600 V for 30 min in all cases. Since one paper strip was required to dissipate 30–40 W, intimate contact with the cooling surface was maintained by an air pressure-bag system. After separation the paper strips were dried and the technetium distribution determined by a radiochromatogram scanner.

Results and discussion

We have recently reported that nitridotechnetic(VI) acid (1) dissolves in weakly-coordinating acids to give the di-(μ -O) bridged aqua cation $[\text{TcN}(\text{OH}_2)_3(\mu\text{-O})_2\text{TcN}(\text{OH}_2)_3]^{2+}$ (4) [6]. Evidence for formulation 4 is the similarity of the UV-Vis spectrum to that of the well established $[\text{Mo}_2\text{O}_4(\text{OH}_2)_6]^{2+}$ cation [7] and reaction with $\text{Na}(\text{S}_2\text{CNET}_2)$ to give the structurally characterised dimer $\{[\text{TcN}(\text{S}_2\text{CNET}_2)]_2(\mu\text{-O})_2\}$ (3) [6]. Further evidence is the electrophoretic migration of 4, 3.9–4.1 cm in 0.5 M Hpts compared to 7.1 cm for $[\text{Cu}(\text{OH}_2)_6]^{2+}$ under the same conditions. This is consistent with formulation 4 but excludes the singly bridged $[\text{TcN}(\text{OH}_2)_4\text{-O-TcN}(\text{OH}_2)_4]^{4+}$ and the monomeric $[\text{TcN}(\text{OH}_2)_5]^{3+}$ species.

Solutions of $\text{Cs}_2[\text{TcNCl}_5]$ in 1 M Hpts, $\text{CF}_3\text{SO}_3\text{H}$ or $\text{CH}_3\text{SO}_3\text{H}$ ($[\text{Tc}] = 0.025$ M) were initially purple-red but became purple-brown on standing. On electrophoresis in 0.5 M acid, the cation 4 was formed due to removal of Cl^- by migration to the anode. When either 1 or $\text{Cs}_2[\text{TcNCl}_5]$ was dissolved in the more strongly coordinating 1 M KHSO_4 solution, electrophoresis in 0.5 M KHSO_4 showed the absence of cationic species and that all the radioactivity was present as an anionic species which migrated ~ 1 cm. Cation 4 and the anionic species are readily interconverted since solutions of $\text{Cs}_2[\text{TcNCl}_5]$ or 1 in 1 M Hpts subjected to electrophoresis in 0.5 M KHSO_4 showed the presence of only the anionic species. Similarly, solutions of $\text{Cs}_2[\text{TcNCl}_5]$ and 1 in 1 M KHSO_4 gave only 4 on electrophoresis in 0.5 M Hpts.

Solutions of 1 in 1 M Hpts, $\text{CF}_3\text{SO}_3\text{H}$ or $\text{CH}_3\text{SO}_3\text{H}$ ($[\text{Tc}] = 2 \times 10^{-3}$ M) exhibited no ESR signals when frozen to 130 K. Addition of conc. HCl (1:1 vol./vol.) to these solutions resulted in the appearance of ESR signals due to $[\text{TcNCl}_4]^-$ with intensities corresponding to all the Tc present. Dissolution of $\text{Cs}_2[\text{TcNCl}_5]$ in 1 M $\text{CF}_3\text{SO}_3\text{H}$ gave ESR signals corresponding to only 5% of the Tc present. These observations are consistent with the formation of diamagnetic dimers in the 1 M acids.

Addition of ethanol to a solution of 1 in 1 M CsOH resulted in the precipitation of the salt $\text{Cs}_2[\text{Tc}_2\text{N}_2\text{O}_2(\text{OH})_4]$ (2). The dimeric formula 2 is supported by the IR spectrum (Fig. 1) which shows the $\nu(\text{Tc}\equiv\text{N})$ absorption at 1046 cm^{-1} and an absorption at 734 cm^{-1} ($\nu_{\text{asym}}(\text{Tc-O-Tc})$) indicating the presence of the $\text{NTc}(\mu\text{-O})_2\text{TcN}$ group. The IR spectrum of 1 is very similar to that of 2 and indicates a structural relationship between these two compounds and $\text{MoO}(\text{OH})_3$, the spectrum of which (Fig. 1) shows broad peaks at 945 cm^{-1} ($\nu(\text{Mo}=\text{O})$) and $\sim 728\text{ cm}^{-1}$ ($\nu(\text{OMo}(\mu\text{-O})_2\text{MoO})\text{ cm}^{-1}$). The UV-Vis spectrum

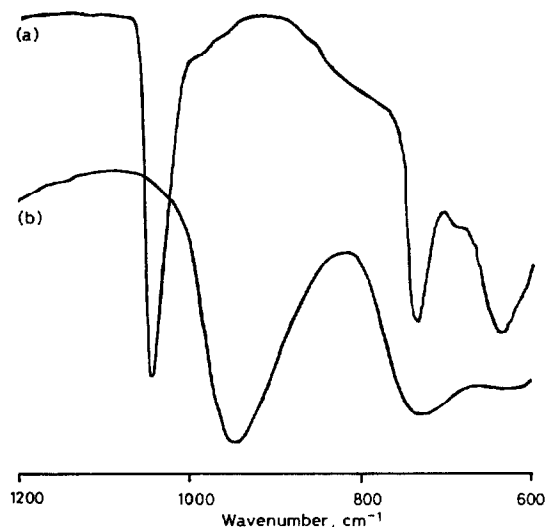


Fig. 1. Infrared spectra of (a) $\text{Cs}_2[\text{Tc}_2\text{N}_2\text{O}_2(\text{OH})_4]$ (2) and (b) $\text{MoO}(\text{OH})_3$.

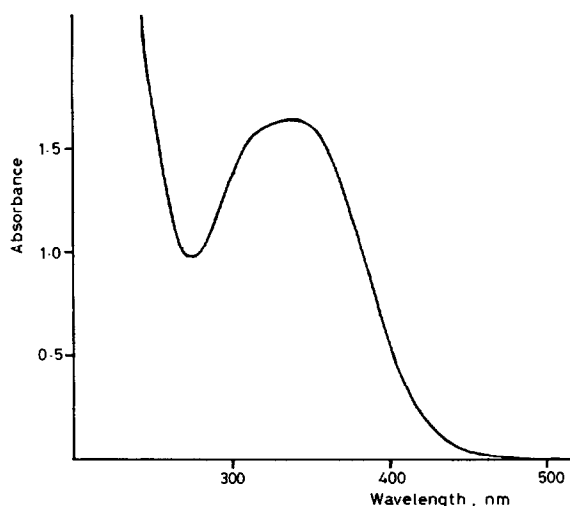


Fig. 2. UV-Vis spectrum of 5×10^{-4} M nitridotechnetic(VI) acid (1) in 0.1 M CsOH .

of 1 in 0.1 M CsOH shows an absorption at 344 nm ($\epsilon = 3270\text{ M}^{-1}\text{ cm}^{-1}$ per dimer) (Fig. 2). When freshly prepared, the salt 2 was readily soluble in water, but aged samples became only partially soluble. Also, solutions of 2 gradually deposited a yellow precipitate. Treatment of 2 with 6 M HCl resulted in conversion to $[\text{TcNCl}_4]^-$ via the deep-blue intermediate which we have previously described [8].

$\text{Cs}_2[\text{TcNCl}_5]$ is soluble in 0.25 M NaOH and in aqueous $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ (saturated at room temperature, ~ 0.14 M) to give yellow solutions. Addition of three equivalents of $\text{Na}(\text{S}_2\text{CNET}_2)$ to the NaOH solution gave a 50% yield of the $\text{Tc}^{\text{VI}}\text{N}$ dimer 3 together with 6% of the reduced $[\text{Tc}^{\text{V}}\text{N}(\text{S}_2\text{CNET}_2)_2]$.

Reaction of 1.5 equiv. of $\text{Na}(\text{S}_2\text{CNET}_2)$ with $\text{Cs}_2[\text{TcNCl}_5]$ in $\text{Na}_4\text{P}_2\text{O}_7$ gave 6% of $[\text{TcN}(\text{S}_2\text{CNET}_2)_2]$ and 59% of **3**. The amount of $\text{Na}(\text{S}_2\text{CNET}_2)$ does not, however, appear to be critical since use of five equivalents (in the $\text{Na}_4\text{P}_2\text{O}_7$ solution) gave 4% of the $\text{Tc}^{\text{VI}}\text{N}$ monomer and 51% of **3**. Reaction of freshly prepared **2** with $\text{Na}(\text{S}_2\text{CNET}_2)$ gave only the dimer **3**. It is pertinent to note that the reaction of $\text{R}[\text{TcNCl}_4]$ with $\text{Na}(\text{S}_2\text{CNET}_2)$ in organic solvents has previously resulted only in the isolation of the reduced $[\text{Tc}^{\text{V}}\text{N}(\text{S}_2\text{CNET}_2)_2]$ complex [3].

No ESR signals were observed from a powder of **3** at temperatures between 130 and 300 K. Similarly no signals were observed from solutions frozen to 130 K of $\text{Cs}_2[\text{TcNCl}_5]$ in $\text{Na}_4\text{P}_2\text{O}_7$ or of **1** in 0.1 M CsOH or $\text{Na}_4\text{P}_2\text{O}_7$ ($[\text{Tc}] = 2 \times 10^{-3}$ M).

The absence of ESR signals and the formation of the dimer **3** are consistent with the formulation of **1** and **2** as the diamagnetic $\text{Tc}^{\text{VI}}\text{N}$ dimeric species $[\text{TcN}(\text{OH})(\text{OH}_2)(\mu\text{-O})_2\text{TcN}(\text{OH})(\text{OH}_2)]$ and $\text{Cs}_2[\text{TcN}(\text{OH})_2(\mu\text{-O})_2\text{TcN}(\text{OH})_2]$, respectively. The aqua cation $[\text{Tc}_2\text{N}_2\text{O}_2(\text{OH}_2)_6]^{2+}$ (**4**) may thus be regarded as a tetraprotic acid with proton loss occurring in two steps to give **1** and then **2**. Similar structures, such as $(\text{NH}_4)_2[\text{Mo}_2\text{O}_4\text{Cl}_2(\text{OH})_2(\text{H}_2\text{O})_2]$ (**5**), have been proposed for Mo^{V} . Aqueous solutions of **5** have been reported to slowly hydrolyse to $\text{MoO}(\text{OH})_3$ [9].

Whilst the dimeric structures for **1** and **2** are consistent with our observations, the alternative polymeric-chain structures such as $[\text{TcN}(\text{OH})(\text{OH}_2)(\mu\text{-O})]_n$ or $[\text{TcN}(\text{OH})(\mu\text{-O})]_n \cdot n\text{H}_2\text{O}$ for **1** (and corresponding structures for the caesium salt **2**) remain possibilities. A soluble polymeric Mo^{VO} aqua ion, of unknown structure, has been described [10]. The hydrated metavanadates, such as $\text{KVO}_3 \cdot \text{H}_2\text{O}$, have been shown to consist of infinite chains of linked VO_5 polyhedra [11].

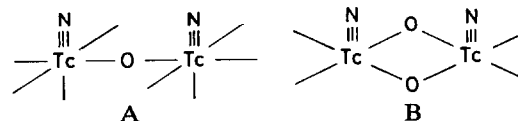
Relationships between Mo^{VO} and $\text{Tc}^{\text{VI}}\text{N}$ chemistries

Addition of hydroxide to acidic solutions containing $[\text{Mo}_2\text{O}_4(\text{OH}_2)_6]^{2+}$ results in the precipitation of $\text{MoO}(\text{OH})_3$ which redissolves on further addition of hydroxide with disproportionation to Mo^{VI} and Mo^{IV} [5]. This is in marked contrast to **1** which does not disproportionate and the caesium salt **2** may be isolated.

Although $\text{MoO}(\text{OH})_3$ has long been used as a starting material for the preparation of Mo^{VO} complexes [12], its structure is uncertain [13]. The IR spectrum of $\text{MoO}(\text{OH})_3$ (Fig. 1) indicates, however, that this compound is either dimeric or polymeric and structurally similar to **1**. It may be noted that dilute aqueous solutions of $\text{K}_2[\text{OsNCl}_5]$ have been reported to slowly decompose to give a brown pre-

cipitate, the nature of which does not appear to have been investigated [14].

The chemistries of $\text{Tc}^{\text{VI}}\text{N}$ and the isoelectronic Mo^{VO} show a marked similarity, as exemplified by the formation of the $[\text{Tc}_2\text{N}_2\text{O}_2(\text{OH}_2)_6]^{2+}$ and $[\text{Mo}_2\text{O}_4(\text{OH}_2)_6]^{2+}$ cations. The two $\text{Tc}^{\text{VI}}\text{N}$ dimeric cores A and B have now been crystallographically



established in the cyclic tetramer $(\text{AsPh}_4)_4\text{-}[\text{Tc}_4\text{N}_4(\text{O})_2(\text{ox})_6]$ ($\text{ox} = \text{oxalate}$) and in **3**, respectively [15, 6]. The nitrido ligands in A are *cis* to the bridging oxygen, as is the case for the terminal oxo ligands in $[\text{Mo}_2\text{O}_3]^{4+}$ complexes [16], and thus differ from the $[\text{OM}^{\text{V}}\text{-O-M}^{\text{VO}}]^{4+}$ ($\text{M} = \text{Tc}, \text{Re}$) dimers where the terminal oxo ligands are *trans* to give an essentially linear geometry [17]. The salt $\text{Cs}_2[\text{TcNCl}_5]$ dissolved in NaOH or $\text{Na}_4\text{P}_2\text{O}_7$ solution has now been shown to provide a convenient method for the preparation of complexes containing the $[\text{Tc}_2\text{N}_2\text{O}_2]^{2+}$ core and we are currently investigating reactions with a variety of ligands.

Although we have not attempted the reaction, it seems likely that nitridotechnetic(VII) acid, $[\text{Tc}(\text{N})\text{O}_3\text{H}_2]$, or its salts, $\text{M}_2[\text{Tc}(\text{N})\text{O}_3]$, could be prepared by the reaction of Tc_2O_7 with liquid ammonia or MNH_2/NH_3 (cf. the reaction of Re_2O_7 to give $\text{K}_2[\text{Re}(\text{N})\text{O}_3]$ [18]). The stability of the $\text{Tc}^{\text{VII}}\text{N}$ core has recently been demonstrated by the preparation of peroxo complexes of the type $\text{R}[\text{TcN}(\text{O}_2)_2\text{X}]$ ($\text{X} = \text{Cl}, \text{Br}$) and $[\text{TcN}(\text{O}_2)_2(\text{L-L})]$ ($\text{L-L} = 2,2'$ -bipyridyl or 1,10-phenanthroline) [19, 4].

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