Inorganica Chimica Acta, *179* (1991) 151–154

Inorganica Chimica Acta
LETTER

Nitridotechnetium(VI) aqueous solution chemistry

John Baldas*, John F. Boas, John Bonnyman, Silvano F. Colmanet and **Geoffrey A. Williams**
Australian Radiation Laboratory, Lower Plenty Road, Yallambie, Vic. 3085 (Australia)

(Received October 15, 1990)

We have recently reported the hydrolysis of $Cs_2[TcNCl_5]$ 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, $[Os(N)O_3H]$ ('osmiamic acid'), and to the hypothetical nitridorhenic(VII) and nitridomolybdic(VI) acids which are known as the $M_2[Re(N)O_3]$ and $M_3[Mo(N)O_3]$ salts, respectively [2]. We now report properties of **1** and of $Cs_2[TcNCl_5]$ which show close parallels, and some significant differences, to those of the isoelectronic '$MoO(OH)_3$' and $M_2[MoOCl_5]$.

Experimental

$Cs_2[TcNCl_5]$ was prepared by the methods described previously [3, 4] and $MoO(OH)_3$ by the addition of NaOH to a solution of $(NH_4)_2[MoOCl_5]$ [5]. Infrared spectra were determined in KBr discs. ESR spectra were obtained by use of a Bruker ESR-200 D spectrometer.

$Cs_2[Tc_2N_2O_2(OH)_4]$ (2)

Nitridotechnetic(VI) acid (**1**) prepared by the hydrolysis of $Cs_2[TcNCl_5]$ (130 mg, 0.234 mmol) was added to a solution of $CsOH \cdot H_2O$ (300 mg, 1.8 mmol) in 1.8 cm^3 of water. The mixture was vigorously shaken and a further 3 cm^3 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 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 $Cs_2[TcNCl_5]$). *Anal.* Calc. for $Cs_2H_4N_2O_6Tc_2$: 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 cm^3 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 cm^3 of water) gave an orange precipitate of $AsPh_4[TcNCl_4]$ which was collected by filtration and washed with 6 M HCl. Yield 24.5 mg (95%).

$[\{TcN(S_2CNEt_2)\}_2(\mu\text{-}O)_2]$ (3)

$Cs_2[TcNCl_5]$ (70 mg, 0.126 mmol) was dissolved with shaking in 4 cm^3 of 0.25 M NaOH to give a yellow–brown solution. On addition of $Na(S_2CNEt_2) \cdot 3H_2O$ (85 mg, 0.38 mmol) in 1 cm^3 of water the mixture became cloudy and a yellow precipitate formed. The mixture was extracted with CH_2Cl_2 (2×4 cm^3) 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 $[TcN(S_2CNEt_2)_2]$ (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), CF_3SO_3H, CH_3SO_3H 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.

---

*Author to whom correspondence should be addressed.

0020-1693/91/$3.50

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 $[TcN(OH_2)_3(\mu\text{-}O)_2TcN(OH_2)_3]^{2+}$ (**4**) [6]. Evidence for formulation **4** is the similarity of the UV–Vis spectrum to that of the well established $[Mo_2O_4(OH_2)_6]^{2+}$ cation [7] and reaction with $Na(S_2CNEt_2)$ to give the structurally characterised dimer $[\{TcN(S_2CNEt_2)\}_2(\mu\text{-}O)_2]$ (**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 $[Cu(OH_2)_6]^{2+}$ under the same conditions. This is consistent with formulation **4** but excludes the singly bridged $[TcN(OH_2)_4\text{–}O\text{–}TcN(OH_2)_4]^{4+}$ and the monomeric $[TcN(OH_2)_5]^{3+}$ species.

Solutions of $Cs_2[TcNCl_5]$ in 1 M Hpts, CF_3SO_3H or CH_3SO_3H ($[Tc]=0.025$ 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 $Cs_2[TcNCl_5]$ 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 $Cs_2[TcNCl_5]$ 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 $Cs_2[TcNCl_5]$ and **1** in 1 M $KHSO_4$ gave only **4** on electrophoresis in 0.5 M Hpts.

Solutions of **1** in 1 M Hpts, CF_3SO_3H or CH_3SO_3H ($[Tc]=2\times10^{-3}$ 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 $[TcNCl_4]^-$ with intensities corresponding to all the Tc present. Dissolution of $Cs_2[TcNCl_5]$ in 1 M CF_3SO_3H 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 $Cs_2[Tc_2N_2O_2(OH)_4]$ (**2**). The dimeric formula **2** is supported by the IR spectrum (Fig. 1) which shows the $\nu(Tc\equiv N)$ absorption at 1046 cm^{-1} and an absorption at 734 cm^{-1} (ν_{asym} (Tc–O–Tc)) indicating the presence of the $NTc(\mu\text{-}O)_2TcN$ group. The IR spectrum of **1** is very similar to that of **2** and indicates a structural relationship between these two compounds and $MoO(OH)_3$, the spectrum of which (Fig. 1) shows broad peaks at 945 $\nu(Mo{=}O)$ and ~728 $\nu(OMo(\mu\text{-}O)_2MoO)$ cm^{-1}. The UV–Vis spectrum of **1** in 0.1 M CsOH shows an absorption at 344 nm ($\epsilon=3270$ M^{-1} 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 $[TcNCl_4]^-$ via the deep-blue intermediate which we have previously described [8].

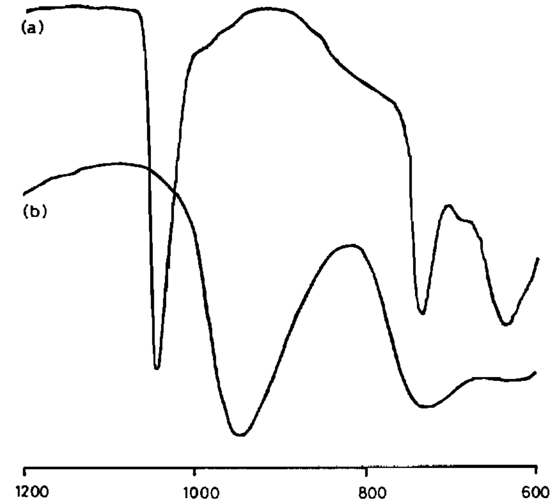


Fig. 1. Infrared spectra of (a) $Cs_2[Tc_2N_2O_2(OH)_4]$ (**2**) and (b) $MoO(OH)_3$.

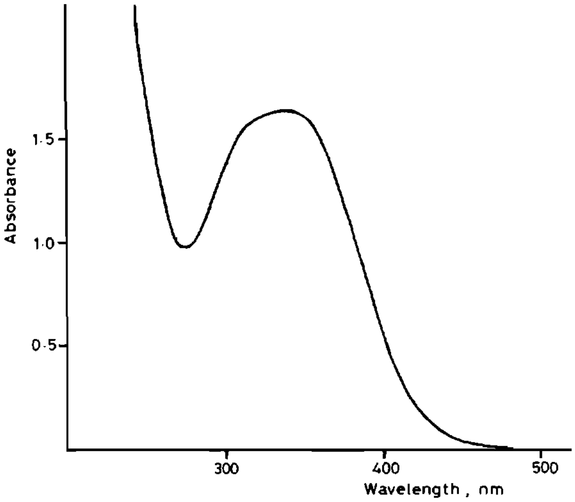


Fig. 2. UV–Vis spectrum of 5×10^{-4} M nitridotechnetic(VI) acid (**1**) in 0.1 M CsOH.

$Cs_2[TcNCl_5]$ is soluble in 0.25 M NaOH and in aqueous $Na_4P_2O_7\cdot10H_2O$ (saturated at room temperature, ~0.14 M) to give yellow solutions. Addition of three equivalents of $Na(S_2CNEt_2)$ to the NaOH solution gave a 50% yield of the $Tc^{VI}N$ dimer **3** together with 6% of the reduced $[Tc^VN(S_2CNEt_2)_2]$.

Reaction of 1.5 equiv. of $Na(S_2CNEt_2)$ with $Cs_2[TcNCl_5]$ in $Na_4P_2O_7$ gave 6% of $[TcN(S_2CNEt_2)_2]$ and 59% of **3**. The amount of $Na(S_2CNEt_2)$ does not, however, appear to be critical since use of five equivalents (in the $Na_4P_2O_7$ solution) gave 4% of the $Tc^{V}N$ monomer and 51% of **3**. Reaction of freshly prepared **2** with $Na(S_2CNEt_2)$ gave only the dimer **3**. It is pertinent to note that the reaction of $R[TcNCl_4]$ with $Na(S_2CNEt_2)$ in organic solvents has previously resulted only in the isolation of the reduced $[Tc^{V}N(S_2CNEt_2)_2]$ 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 $Cs_2[TcNCl_5]$ in $Na_4P_2O_7$ or of **1** in 0.1 M CsOH or $Na_4P_2O_7$ ($[Tc]=2\times10^{-3}$ 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 $Tc^{VI}N$ dimeric species $[TcN(OH)(OH_2)(\mu\text{-}O)_2TcN(OH)(OH_2)]$ and $Cs_2[TcN(OH)_2(\mu\text{-}O)_2TcN(OH)_2]$, respectively. The aqua cation $[Tc_2N_2O_2(OH_2)_6]^{2+}$ (**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 $(NH_4)_2[Mo_2O_4Cl_2(OH)_2(H_2O)_2]$ (**5**), have been proposed for Mo^{V}. Aqueous solutions of **5** have been reported to slowly hydrolyse to $MoO(OH)_3$ [9].

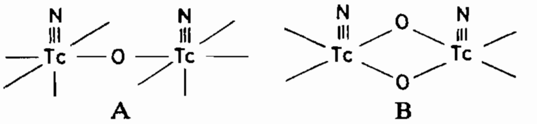
Whilst the dimeric structures for **1** and **2** are consistent with our observations, the alternative polymeric-chain structures such as $[TcN(OH)(OH_2)(\mu\text{-}O)]_n$ or $[TcN(OH)(\mu\text{-}O)]_n\cdot nH_2O$ for **1** (and corresponding structures for the caesium salt **2**) remain possibilities. A soluble polymeric $Mo^{V}O$ aqua ion, of unknown structure, has been described [10]. The hydrated metavanadates, such as $KVO_3\cdot H_2O$, have been shown to consist of infinite chains of linked VO_5 polyhedra [11].

Relationships between $Mo^{V}O$ and $Tc^{VI}N$ chemistries

Addition of hydroxide to acidic solutions containing $[Mo_2O_4(OH_2)_6]^{2+}$ results in the precipitation of $MoO(OH)_3$ 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 $MoO(OH)_3$ has long been used as a starting material for the preparation of $Mo^{V}O$ complexes [12], its structure is uncertain [13]. The IR spectrum of $MoO(OH)_3$ (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 $K_2[OsNCl_5]$ have been reported to slowly decompose to give a brown precipitate, the nature of which does not appear to have been investigated [14].

The chemistries of $Tc^{VI}N$ and the isoelectronic $Mo^{V}O$ show a marked similarity, as exemplified by the formation of the $[Tc_2N_2O_2(OH_2)_6]^{2+}$ and $[Mo_2O_4(OH_2)_6]^{2+}$ cations. The two $Tc^{VI}N$ dimeric cores A and B have now been crystallographically established in the cyclic tetramer $(AsPh_4)_4$-$[Tc_4N_4(O)_2(ox)_6]$ (ox = 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 $[Mo_2O_3]^{4+}$ complexes [16], and thus differ from the $[OM^{V}\text{–}O\text{–}M^{V}O]^{4+}$ (M = Tc, Re) dimers where the terminal oxo ligands are *trans* to give an essentially linear geometry [17]. The salt $Cs_2[TcNCl_5]$ dissolved in NaOH or $Na_4P_2O_7$ solution has now been shown to provide a convenient method for the preparation of complexes containing the $[Tc_2N_2O_2]^{2+}$ 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, $[Tc(N)O_3H_2]$, or its salts, $M_2[Tc(N)O_3]$, 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 $K_2[Re(N)O_3]$ [18]). The stability of the $Tc^{VII}N$ core has recently been demonstrated by the preparation of peroxo complexes of the type $R[TcN(O_2)_2X]$ (X = Cl, Br) and $[TcN(O_2)_2(L\text{-}L)]$ (L-L = 2,2′-bipyridyl or 1,10-phenanthroline) [19, 4].

References

1 J. Baldas, J. F. Boas and J. Bonnyman, *Aust. J. Chem., 42* (1989) 639.
2 W. P. Griffith, *Coord. Chem. Rev., 8* (1972) 369.
3 J. Baldas, J. Bonnyman and G. A. Williams, *Inorg. Chem., 25* (1986) 150.
4 J. Baldas and S. F. Colmanet, *Inorg. Chim. Acta, 176* (1990) 1.
5 P. Souchay, M. Cadiot and B. Viossat, *Bull. Soc. Chim. Fr.,* (1970) 892.
6 J. Baldas, J. F. Boas, J. Bonnyman, S. F. Colmanet and G. A. Williams, *J. Chem. Soc., Chem. Commun.,* (1990) 1163.
7 M. Ardon and A. Pernick, *Inorg. Chem., 12* (1973) 2484; Y. Sasaki and A. G. Sykes, *J. Chem. Soc., Dalton Trans.,* (1974) 1468.
8 J. Baldas and J. F. Boas, *J. Chem. Soc., Dalton Trans.,* (1988) 2585.

9 B. Jezowska-Trzebiatowska, M. F. Rudolf, L. Natkaniec and H. Sabat, *Inorg. Chem., 13* (1974) 617.

10 F. A. Armstrong and A. G. Sykes, *Polyhedron, 1* (1982) 109.

11 C. L. Christ, J. R. Clark and H. T. Evans, Jr., *Acta Crystallogr., 7* (1954) 801.

12 W. G. Palmer, *Experimental Inorganic Chemistry*, Cambridge University Press, London, 1965, p. 406.

13 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley-Interscience, New York, 1988, p. 808.

14 A. F. Clifford and C. S. Kobayashi, *Inorg. Synth., 6* (1960) 204.

15 J. Baldas, S. F. Colmanet and M. F. Mackay, *J. Chem. Soc., Dalton Trans.*, (1988) 1725.

16 E. I. Stiefel, *Prog. Inorg. Chem., 22* (1977) 1.

17 F. Tisato, F. Refosco, U. Mazzi, G. Bandoli and A. Dolmella, *Inorg. Chim. Acta, 164* (1989) 127; M. R. A. Pillai, C. S. John, J. M. Lo, E. O. Schlemper and D. E. Troutner, *Inorg. Chem., 29* (1990) 1850.

18 A. F. Clifford and R. R. Olsen, *Inorg. Synth., 6* (1960) 167.

19 J. Baldas, S. F. Colmanet and M. F. Mackay, *J. Chem. Soc., Chem. Commun.*, (1989) 1890.