

## Preparation and Structure of $[\{\text{Tc}^{\text{V}}\text{N}(\text{thiourea})\}_4(\text{edta})_2]\cdot 6\text{H}_2\text{O}$ : the First Example of a Cyclic Nitrido-bridged Tetrameric Technetium Complex

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The complex  $[\{\text{Tc}^{\text{V}}\text{N}(\text{thiourea})\}_4(\text{edta})_2]\cdot 6\text{H}_2\text{O}$  has been prepared and is shown to consist of a cyclic tetrameric  $\text{Tc}_4\text{N}_4$  configuration with four asymmetrical  $\text{Tc}\equiv\text{N}-\text{Tc}$  bridges; each diagonal pair of Tc atoms is bridged by an  $\text{edta}^{4-}$  ligand and  $\text{Tc}\equiv\text{N}$  distances range between 1.681(7) and 1.695(7) Å, with  $\text{N}-\text{Tc}$  of 1.977(7) to 2.009(7) Å.

Recently, we reported the first structural characterisation of a nitrido-bridged technetium complex,  $[\text{Cs}(18\text{-crown-6})][\text{TcNCl}_4]$ , containing polymeric  $[\text{Tc}^{\text{V}}\text{NCl}_4]^-$  anions.<sup>1,2</sup> The structure consists of an 'infinite sandwich'  $\text{Cs}^+$  cation/crown ether configuration and anti-parallel linear chains of  $-\text{Tc}\equiv\text{N}-\text{Tc}\equiv\text{N}-$  with  $\text{Tc}\equiv\text{N}$  distances of 1.56(4) Å and  $\text{Tc}\cdots\text{Tc}$  separations of 4.275(4) Å. Also, two  $[\text{M}(18\text{-crown-6})]^+$  ( $\text{M} = \text{Cs}, \text{H}_3\text{O}$ ) salts containing dimeric  $[\text{N}\equiv\text{TcCl}_4\cdots\text{N}\equiv\text{Tc}(\text{OH}_2)\text{Cl}_4]^{2-}$  anions have recently been prepared and structurally characterised.<sup>3</sup> In these dimeric anions, the  $\text{N}\equiv\text{Tc}\cdots\text{N}\equiv\text{Tc}$  bonding is linear and distinctly asymmetrical.

The tetrameric rectangular bonding system **1**, while common for metals such as  $\text{M} = \text{Mo}, \text{W}$  and  $\text{Re}$ ,<sup>4</sup> has not before been observed for Tc.

Typical examples of such tetrameric nitrido-bridged systems are provided by  $[\text{MoNCl}_3\{\text{O}(\text{C}_4\text{H}_9)_2\}_2]_4$ ,<sup>5</sup> in which the alternating  $\text{Mo}-\text{N}$  distances are 1.65 and 2.16 Å, and the  $[\text{W}_4\text{N}_4\text{Cl}_{14}(\text{CH}_3\text{CN})_2]^{2-}$  anion in which the  $\text{W}-\text{N}$  bonding is again asymmetrical with distances 1.68 and 2.10 Å.<sup>6</sup> In both these cases, the metal atoms are located at the corners of a square, and are linked *via* nearly linear  $\text{M}\equiv\text{N}-\text{M}$  bridges.

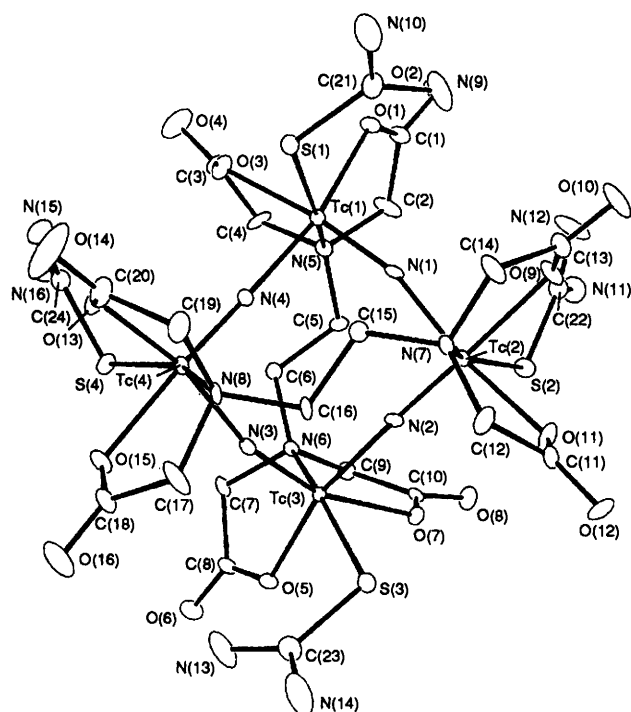
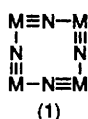


Fig. 1 The structure of  $[\{\text{TcN}(\text{tu})\}_4(\text{edta})_2]$ ; thermal ellipsoids are drawn at the 25% probability level

In the tetranuclear  $\text{Mo}^{\text{V}}$  complex  $[\text{MoN}\{\text{S}_2\text{P}(\text{OMe})_2\}_2]_4$ ,<sup>7</sup> the  $[\text{MoN}]_4$  core is essentially square and planar; however, in this example the  $\text{Mo}-\text{N}$  bonding is symmetrical with equivalent  $\text{Mo}-\text{N}$  bond lengths of *ca.* 1.87 Å.

The title complex,  $[\{\text{Tc}^{\text{V}}\text{N}(\text{tu})\}_4(\text{edta})_2]\cdot 6\text{H}_2\text{O}$  ( $\text{tu} = \text{thiourea}$ ), was prepared in low yield by the addition of  $[\text{TcN}(\text{tu})_4\text{Cl}]\text{Cl}$  to an aqueous solution of  $\text{Na}_2\text{H}_2\text{edta}$ . After leaving to stand at ambient temperature for several days, the resultant brown solution yielded deep-brown crystals suitable for X-ray diffraction studies.† The crystals are insoluble in water and in organic solvents such as ethanol, acetonitrile, dichloromethane and dimethylformamide (dmf). The IR spectrum shows strong peaks at 1681 $[\nu(\text{CO})]$  and 1632 $[\delta(\text{H}_2\text{O})]$ , and a medium peak at 984  $\text{cm}^{-1}$  is assigned to  $\nu(\text{Tc}\equiv\text{N})$ . The low value of  $\nu(\text{Tc}\equiv\text{N})$  is consistent with a bridging nitrido ligand in the presence of a *trans* ligand. A suspension of  $[\{\text{Tc}^{\text{V}}\text{N}(\text{tu})\}_4(\text{edta})_2]\cdot 6\text{H}_2\text{O}$  in dmf reacted slowly with  $\text{Na}(\text{S}_2\text{CNET}_2)$  to yield the well-known  $[\text{TcN}(\text{S}_2\text{CNET}_2)_2]$ .<sup>8</sup>

The reaction of  $[\text{TcOCl}_4]^-$  with  $\text{H}_4\text{edta}$  has been shown to yield the monomeric seven coordinate  $[\text{TcO}(\text{edta})]^-$  anion.<sup>9</sup> Substitution reactions of  $[\text{TcN}(\text{tu})_4\text{Cl}]\text{Cl}$  have previously resulted in replacement of all the thiourea ligands,<sup>10</sup> and it was a surprise that reaction with  $\text{H}_2\text{edta}^{2-}$  did not yield the  $[\text{Tc}^{\text{V}}\text{N}(\text{edta})]^{2-}$  anion. The reaction of  $[\text{TcNCl}_4]^-$  with  $\text{Na}_2\text{H}_2\text{edta}$  has been reported to yield  $[\text{Tc}^{\text{V}}\text{N}(\text{Hedta})]\cdot 3\text{H}_2\text{O}$ ,<sup>11</sup> but the electronic spectrum of the product indicates that this may be a  $\text{Tc}^{\text{V}}\text{N}-\mu\text{-oxo}$  dimer.<sup>12</sup> The most likely route to the formation of the tetramer,  $[\{\text{TcN}(\text{tu})\}_4(\text{edta})_2]$ , is *via* the coupling of two dimeric  $\text{TcN}(\text{tu})\text{-edta-TcN}(\text{tu})$  units. The considerable stability of the tetramer appears to be due to the 'clamping effect' of the bridging edta ligands and the need to break four  $\text{Tc}-\text{N}_{\text{nitrido}}$  bonds for dissociation to occur.

The crystal structure determination showed a new cyclic tetrameric configuration for technetium with four asymmetrical  $\text{Tc}\equiv\text{N}-\text{Tc}$  bridges and with each diagonal pair of technetium atoms bridged by an  $\text{edta}^{4-}$  ligand (Fig. 1), one edta over and the other under the  $\text{Tc}_4\text{N}_4$  core resulting in an open cage-like structure. The  $\text{Tc}(n)\equiv\text{N}(n)$  distances are

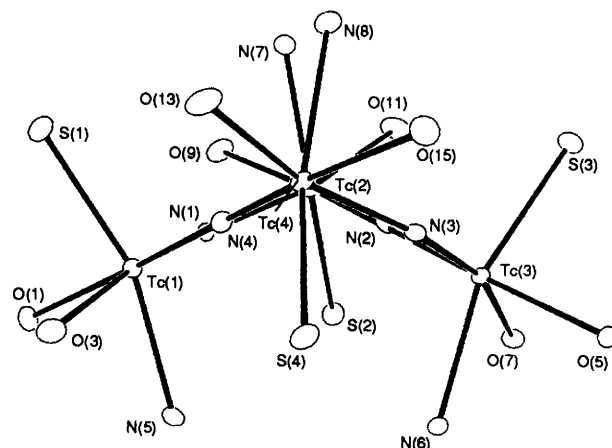


Fig. 2 A view of the Tc coordination spheres in  $[\{\text{TcN}(\text{tu})\}_4(\text{edta})_2]$ , showing the V-shaped conformation of the  $\text{Tc}_4\text{N}_4$  core

1.692(7), 1.694(7), 1.695(7) and 1.681(7) Å, with N(*n*)-Tc distances of 1.977(7), 2.001(7), 1.982(7) and 2.009(7) Å for *n* = 1–4, respectively.

The [TcN]<sub>4</sub> core is not planar, and, viewed down either diagonal Tc...Tc vector, is V-shaped (Fig. 2) with dihedral angles between planes Tc(1) Tc(2) Tc(3) N(1) N(2)/Tc(1) Tc(3) Tc(4) N(3) N(4) 54.2(1)° and Tc(1) Tc(2) Tc(4) N(1) N(4)/Tc(2) Tc(3) Tc(4) N(2) N(3) 52.8(1)°. The Tc(*n*)≡N(*n*)-Tc bonds are close to linear, with angles 163.2(4), 176.6(4), 164.3(4) and 178.6(4)°, and N(*n*)≡Tc(*n*)-N angles are 91.0(3), 90.4(3), 88.5(3) and 91.6(3)° for *n* = 1–4, respectively.

The coordination geometry about each Tc atom is distorted octahedral, with the triply-bonded nitrido ligand in an axial position and each Tc displaced from the equatorial plane towards this ligand. The equatorial atoms are closely planar with Tc displacements of 0.260(3), 0.247(3), 0.264(3) and 0.323(3) Å for Tc(1–4), respectively. The *trans* influence of the nitrido ligands is also apparent in the Tc-O bond distances, with average Tc-O<sub>cis</sub> 2.07 and Tc-O<sub>trans</sub> 2.14 Å.

The hexadentate edta ligands bridge pairs of diagonal technetium atoms, with the carboxylate oxygens in the appropriate Tc<sub>3</sub>N<sub>2</sub> planes and the N atoms of the edta ligands normal to these planes and approximately *trans* to the thiourea S atoms. This mode of edta bridging has the effect of tying the Tc<sub>4</sub>N<sub>4</sub> core together, and presumably makes dissociation difficult. As in the [Tc(tu)<sub>6</sub>]<sup>3+</sup> cation,<sup>15</sup> the thiourea ligands coordinate through essentially sp<sup>2</sup>-hybridised sulfur, with deviations from planarity of each N<sub>2</sub>C=S-Tc system resulting from steric interactions between a hydrogen atom on the nitrogen atom *cis* to technetium and the sulfur atom (Tc-S=C angles 108.7(4)–115.9(4)°, N-C=S angles *cis* to Tc 5.8–7.6° greater than the corresponding *trans* angles).

The crystal structure contains an extensive hydrogen-bonding network involving the lattice water molecules, together with either the amine groups of the thiourea ligands or carboxylate oxygens of edta.

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### Footnote

† Crystal data for [(TcN(tu))<sub>4</sub>(edta)<sub>2</sub>]-6H<sub>2</sub>O: C<sub>24</sub>H<sub>52</sub>N<sub>16</sub>O<sub>22</sub>S<sub>4</sub>Tc<sub>4</sub>, *M* = 1440.66, monoclinic, space group *P*2<sub>1</sub>, *a* = 16.374(2), *b* = 12.525(1), *c* = 12.205(1) Å, β = 107.77(1)°, *U* = 2383.63 Å<sup>3</sup>, *Z* = 2,

*F*(000) = 1440, *D*<sub>c</sub> = 2.007 g cm<sup>-3</sup>, μ = 11.7 mm<sup>-1</sup>. Intensity data were measured within the limit (sinθ)/λ ≤ 0.613 Å<sup>-1</sup> at 23(1) °C with nickel-filtered Cu-Kα radiation (λ = 1.5418 Å) on an automatic Siemens AED diffractometer. The crystal had well-developed faces of type (100), (010), and (001) with perpendicular distances between faces of 0.05, 0.19, and 0.39 mm, respectively. Data were corrected for absorption (transmission factors ranged between 0.14 and 0.62). The structure was solved by the heavy-atom method (SHELXS program<sup>13</sup>), and hydrogen atoms were included at calculated positions. Full-matrix least-squares refinement (SHELXL-93 program<sup>14</sup>) based on *F*<sub>o</sub><sup>2</sup> {function Σ[w(*F*<sub>o</sub><sup>2</sup> - *F*<sub>c</sub><sup>2</sup>)<sup>2</sup>] minimised} converged with *R*(*F*) = 0.034 for 4546 observed terms [*I* > 2σ(*I*)], and *wR*<sub>2</sub> = {Σ[w(*F*<sub>o</sub><sup>2</sup> - *F*<sub>c</sub><sup>2</sup>)<sup>2</sup>]/Σ[w(*F*<sub>o</sub><sup>2</sup>)<sup>2</sup>]}<sup>1/2</sup> = 0.084, χ(*F*<sup>2</sup>) = 1.06 for all 4783 data. The weighting scheme was *w* = [σ<sup>2</sup>(*F*<sub>o</sub><sup>2</sup>) + 0.057*P*<sup>2</sup> + 2.11*P*]<sup>-1</sup> where *P* = 0.33max(*F*<sub>o</sub><sup>2</sup>, 0) + 0.67*F*<sub>c</sub><sup>2</sup>. The largest peaks on a final difference synthesis were of heights 1.0 and -1.1 e Å<sup>-3</sup>. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

### References

- J. Baldas, S. F. Colmanet and G. A. Williams, *J. Chem. Soc., Chem. Commun.*, 1991, 954.
- J. Baldas, J. F. Boas, S. F. Colmanet, A. D. Rae and G. A. Williams, *Proc. R. Soc. London, A*, 1993, **442**, 437.
- J. Baldas, S. F. Colmanet, D. C. Craig, A. D. Rae and G. A. Williams, unpublished results.
- K. Dehnicke and J. Strähle, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 413.
- U. Müller, R. Kujanek and K. Dehnicke, *Z. Anorg. Allg. Chem.*, 1982, **495**, 127.
- A. Neuhaus and K. Dehnicke, *Z. Anorg. Allg. Chem.*, 1993, **619**, 775.
- M. E. Noble, K. Folting, J. C. Huffman and R. A. D. Wentworth, *Inorg. Chem.*, 1982, **21**, 3772.
- J. Baldas, J. Bonnyman, P. M. Pojer, G. A. Williams and M. F. Mackay, *J. Chem. Soc., Dalton Trans.*, 1981, 1798.
- G. Bandoli, U. Mazzi, E. Roncari and E. Deutsch, *Coord. Chem. Rev.*, 1982, **44**, 191.
- J. Baldas and J. Bonnyman, *Inorg. Chim. Acta*, 1988, **141**, 153.
- T. Takayama, T. Sekine and K. Yoshihara, *J. Radioanal. Nucl. Chem., Letters*, 1993, **176**, 325.
- J. Baldas, J. F. Boas, Z. Ivanov and B. D. James, *Inorg. Chim. Acta*, 1993, **204**, 199.
- G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.
- G. M. Sheldrick, SHELXL-93 program for crystal structure refinement, University of Göttingen, 1993.
- M. J. Abrams, A. Davison, R. Faggiani, A. G. Jones and C. J. L. Lock, *Inorg. Chem.*, 1984, **23**, 3284.