Preparation and Structure of [Cs(18-crown-6)][TcNCl$_4$]† —an 'Infinite Sandwich' Cs$^+$–Crown Ether Complex containing Polymeric [TcNCl$_4$]$^-$ Anions

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The compound [Cs(18-crown-6)] [TcNCl$_4$] is prepared and is shown to consist of an 'infinite sandwich' Cs$^+$ cation/crown ether configuration and two types of polymeric [TcNCl$_4$]$^-$ anions, with distinct Tc≡N distances of 1.56(3) and 1.693(5) Å, and Tc≡N···Tc separations of 4.275(4) Å.

There has been much interest in recent years in theoretical, synthetic and spectroscopic studies of transition metal linear-chain nitrido-bridged polymers. Structural studies of the polymeric [ReNCl$_4$],[1] [MN(OR)$_3$] (M = Mo, W)[2,3] and [VNCl$_2$(pyridine)$_2$][4] have shown that the alternating bond lengths in the ···M≡N···M≡N··· backbones are highly asymmetric. A particular interest in these polymers is that the alternating metal–nitrogen bond system may be regarded as an inorganic analogue of the polyacetylenes.[5]

Technetium has been shown to form a large number of stable complexes containing the Tc≡N core with the metal in the +5, 6 or 7 oxidation state. Oxo-bridged complexes such as [{TcN(S$_2$CNEt$_2$)}$_2$(μ-O)$_2$] have been described[6] but, to date, no nitrido-bridged species have been reported. We now report the preparation and structure of [Cs(18-crown-6)][TcNCl$_4$], a

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† 18-Crown-6 = 1,4,7,10,13,16-hexaoxacyclooctadecane

complex containing two types of polymeric $[TcNCl_4]^-$ anions and the unprecedented 'infinite sandwich' alkali-metal cation/crown ether complexation.

[Cs(18-crown-6)][$TcNCl_4$] was prepared by the addition of 18-crown-6 to a suspension of $Cs_2[TcNCl_5]$ in thionyl chloride. The resulting solution was allowed to evaporate at room temperature. The residue was extracted with absolute ethanol to leave a quantitative yield of orange–red crystals suitable for X-ray crystallographic analysis.‡

The tetragonal unit cell of [Cs(18-crown-6)][$TcNCl_4$] (Fig. 1), with $Z = 4$, is a square of 22.46 Å edge length with a tetragonal (c) axis length of 4.275 Å. The Cs^+ cations occupy sites at the corners of the unit cell, at mid-points along the square edges, and in the centres of the squares (*i.e.* at $z = 0$ and 1). Each 18-crown-6 molecule lies more or less in the xy plane at *ca.* $z = ½$, with a Cs^+ cation above and below forming the 'infinite sandwich' array. There are two distinct pairs of anti-parallel chains of $\cdots Tc{\equiv}N\cdots Tc{\equiv}N\cdots$ in the lattice in the cavities at ($\pm ¼, \pm ¼, z$), with the Cl atoms at *ca.* $z = 0$. One pair of chains is disordered over two alternative configurations, with the independent N atom fixed at the special position ($¼, -¼, ½$) and the Tc atom equally disordered over positions ($¼, -¼, \pm z$) giving, in one case, a Tc≡N bond and in the other, a Tc···N bond. In one polymeric chain Tc≡N is 1.56(3) Å and Tc···N is 2.72(3) Å, and in the other (disordered) chain Tc≡N is 1.693(5) Å and Tc···N 2.58(1) Å. Refinement based on all data gave the Tc≡N distances 1.59(2) and 1.693(3) Å, respectively.

Generally, the C–C bond lengths in crown ether complexes determined by X-ray crystallography are found to be less than the reference value of 1.523 Å.[7] This shortening has been ascribed to an artificial effect arising from curvilinear vibrations.[7] During refinement of the structure of [Cs(18-crown-6)][$TcNCl_4$], we observed that both the C–C and C–O bonds were significantly shorter than the expected values. An examination of residual electron density features showed the crown ether to be unequally disordered [61(1)%] over two closely separated positions related by a non-crystallographic mirror plane at $z = ½$. Inclusion of this disorder in the scattering model gave significant improvement in the C–C and C–O bond distances.

In an early paper, Pedersen[8] noted that 2 : 1 and 3 : 2 crown ether : alkali metal cation complexes might consist of a 'sandwich' (crown-M^+-crown) or 'club sandwich' (crown-M^+-crown-M^+-crown) arrangement, respectively, in the solid state. Structural studies have confirmed the 'sandwich' structure for 2 : 1 complexes but the 'club sandwich' structure has only been observed in $[Cs_9(18\text{-crown-}6)_{14}]^{9+}[Rh_{22}(CO)_{35}H_x]^{5-}[Rh_{22}(CO)_{35}H_{x+1}]^{4-}$ where the cation array consists of $[Cs(18\text{-crown-}6)]^+$, $[Cs(18\text{-crown-}6)_2]^+$ and $[Cs_2(18\text{-crown-}6)_3]^{2+}$ units.[9] The possibility of larger 'sandwiches', and in particular of the 1 : 1 'infinite sandwich', does not appear to have been considered, presumably because of the restriction imposed on the position of the counter anion which would be required to be located 'side on' rather than 'end on'.

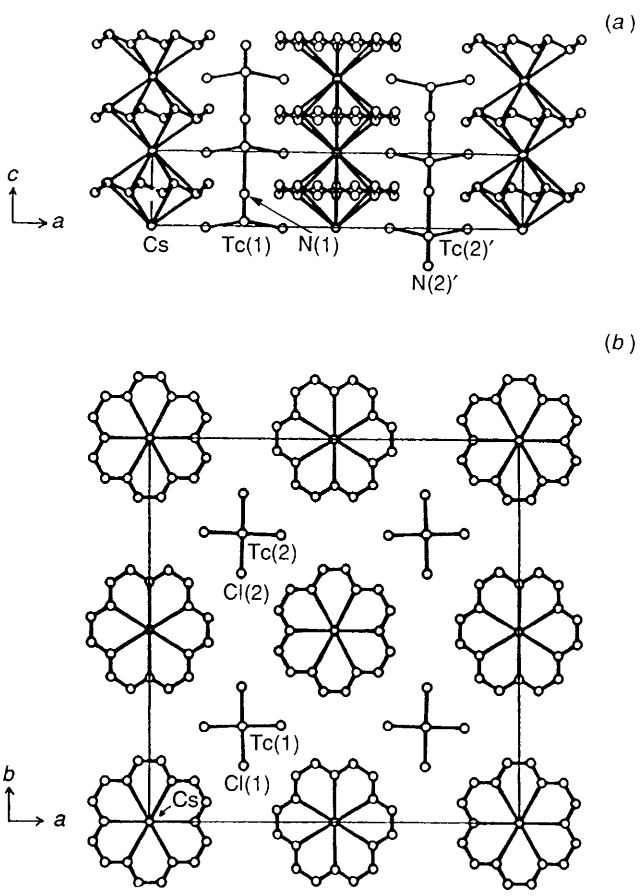

Fig. 1 The crystal structure of [Cs(18-crown-6)][$TcNCl_4$] viewed down the b axis (a) and c axis (b). Atoms are shown by circles of arbitrary size. The Tc(2) chains are disordered with half as shown and the others antiparallel. Only the major component of the disordered crown ether molecule is shown. Selected distances (Å): Tc(1)–Cl(1) 2.336(4), Tc(2)–Cl(2) 2.359(4), Cs–O 3.34(1), 3.67(1), 3.35(1), 3.66(1), 3.34(1), 3.68(1). The N≡Tc–Cl angles are 99.5(2)° for Tc(1) and 100.8(2)° for Tc(2).

The [Cs(18-crown-6)][$TcNCl_4$] lattice has several unusual aspects, all associated with the short cell length of 4.275 Å, and it is of interest to query why such a crystal structure should, indeed, exist. For instance, each Cs^+ cation has two Cs^+ neighbours at 4.275 Å, whereas the Tc atoms of the four nearest anions are at 7.95 Å. In contrast, in CsBr each Cs^+ cation has six nearest cations at a similar distance of 4.29 Å but with eight nearest anions at 3.72 Å.[10] Presumably Cs^+–crown ether bonding and the dielectric nature of the crown ether interspersed between columns of Cs^+ cations are significant in effectively reducing the electrostatic repulsion. The $Cs^+\cdots Cs^+$ separation in the 'infinite sandwich' array is also less than that of 4.658 Å in the less-compressed 'club sandwich' example,[9] where the Cs–O distances to the 'bridging' crown ether are also generally longer [3.29(8) to 4.25(8) Å]. It is difficult to see the weak $\cdots Tc{\equiv}N\cdots Tc{\equiv}N\cdots$ interactions as being responsible for the compression of the Cs^+–crown ether 'infinite sandwich' arrangement, with the Tc≡N···Tc separation a little less than the M≡N···M separations of 4.52 Å for M = Mo,[2] 4.401 Å for M = W,[3] and 4.300 Å for M = V,[4] but longer than the 4.057 Å for M = Re.[1] All of these other separations are found in neutral species, without constraints due to the presence of alkali metal cation/crown ether complexes in the lattice.

In the asymmetric unit of [Cs(18-crown-6)][$TcNCl_4$] there are two crystallographically independent $[TcNCl_4]^-$ anions, with distinctly different Tc≡N bond distances. These differences are supported by the observation of two Tc≡N stretching frequencies (1041 and 1060 cm^{-1}) in the IR spectrum. For the

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‡ *Crystal data* for [Cs(18-crown-6)][$TcNCl_4$]: $C_{12}H_{24}Cl_4CsNO_6Tc$, $M = 651.95$, tetragonal, space group $P4/n$, $a = 22.459(13)$, $c = 4.275(4)$ Å, $U = 2156.3$ Å^3, $Z = 4$, $D_c = 2.008$ g cm^{-3}, $\mu = 22.6$ mm^{-1}. Intensity data were measured at 24(1) °C with nickel-filtered Cu-Kα radiation ($\lambda = 1.5418$ Å) on an automatic Siemens AED diffractometer. The crystal had well-developed faces of type (110), ($\bar{1}$10), and (001) with perpendicular distances between faces of 0.09, 0.10 and 0.38 mm respectively. Data were corrected for absorption. The structure was solved by the heavy-atom method, and hydrogen atoms were included at calculated positions. Full-matrix least-squares refinement with SHELX-76 converged with $R = 0.074$, $R_w = 0.058$, and $\chi = 2.81$ for 1013 observed terms [$I > 3\sigma(I)$]. The largest peaks on a final difference synthesis were of heights 1.0 and -1.8 eÅ^{-3}. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Data Centre. See Notice to Authors, Issue No. 1.

past 20 years, molecules that differ only in the length of one or more bonds have been described as 'distortional isomers'[11] or, alternatively, as 'bond-stretch isomers'.[12] Generally, such isomers contain M=O bonds, one of which is of normal length and the other long (typically 1.8 Å or more).[13]

Recently, the apparent long M=O bond in the green form of *cis-mer*-[$MoOCl_2(PMe_2Ph)_3$] has been shown to result from cocrystallisation of the blue complex [with Mo=O 1.675(3) Å] with a small amount of the yellow impurity, *mer*-[$MoCl_3(PMe_2Ph)_3$].[14] More generally, it was suggested that the observation of long metal–oxo bond lengths should be interpreted with caution. We had arrived at a similar conclusion, based on observations of cases of intramolecular disorder, which, if inadequately treated in the scattering model, give rise to apparently longer than normal M=O or M≡N distances. Such examples, that are to be discussed in detail elsewhere,[15] can involve disorder between the oxo or nitrido ligand and a *trans* ligand, and/or disorder of the central metal atom about a crystallographic symmetry position {as in [$TcN(NCS)_4(CH_3CN)]^{2-}$}.[15] Other parameters of the refinement, such as choice of weighting scheme, can also have a marked effect on the apparent M=O and M≡N distances. We would suggest that if bond-stretch isomerism is to survive as a credible concept, it will involve differences in bond lengths of smaller magnitude than previously thought, and some corroborating evidence (such as IR stretching frequencies) should be available to support the X-ray crystallography.

It is possible that the difference in Tc≡N bond distances observed within the cell of [Cs(18-crown-6)][$TcNCl_4$] is real, and, therefore, an authentic example of bond-stretch isomerism. This is supported by the observation of two Tc≡N stretches in the IR spectrum (although other solid-state effects can give a similar result[16]), and by the fact that the two bond distances remain well-separated upon changing various refinement parameters. Most doubt is raised by the position of the nitrido N atom in the disordered polymeric chain, which is on a site of $\bar{4}$ symmetry. An examination of electron-density maps showed an elongated density in the *z* direction at this position, but refinement with this nitrogen disordered over two closely related positions on either side of the special position of symmetry yielded a less satisfactory model.

The related [Rb(18-crown-6)][$TcNCl_4$] has been prepared and shows only a single ν(Tc≡N) absorption at 1074 cm^{-1} {*cf.* ν(Tc≡N) 1076 cm^{-1} for ($AsPh_4$)[$TcNCl_4$]} indicating that the [$TcNCl_4$]$^-$ anions in this compound are not polymeric.

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