

In the trichloride complex, the nitrile ligands are bent at a small angle from the $Ru(NCR)_3$ plane but in opposing directions rather than nesting in a propeller conformation.

Metal–ligand bond lengths. The average $Ru–Cl$ bond distance for chloride *trans* to chloride in $RuCl_3(C_6H_5CN)_3$ is 2.324 Å, while the $Ru–Cl$ distance of chloride *trans* to benzonitrile is significantly shorter (2.293 Å). Similarly, the $Ru–N$ bond for nitrile *trans* to chloride (2.060 Å) is longer than it is for the two mutually *trans* nitriles (2.010 Å average). Both observations are in accord with the ‘*trans* influence’ of chloride being greater than that of benzonitrile. The only other structural determination of a ruthenium(III) nitrile complex is for the lower-symmetry species acetonitrile-*mer*-trichloro[1-methyl-3-(2-pyridyl)-1,2,4-triazole-*N*(4),*N*(1')]ruthenium (Hage, Prins, de Graaff, Haasnoot, Reedijk & Vos, 1988) where the $Ru–N$ bond distance is

2.034 Å for acetonitrile *trans* to the pyridyl fragment of the bidentate ligand.

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{2,2'-Dimethyl-1,1'-[(*N,N'*-²H₂)-ethylenediamino]dipropane-2-thiolato-*N,N',S,S'*}-oxotechnetium(V) Chloride Monodeuterate

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Abstract. $[Tc(C_{10}H_{20}D_2N_2S_2)(O)]Cl.D_2O$, $M_r = 406.8$, monoclinic, $P2_1/c$, $a = 6.160$ (2), $b = 26.727$ (6), $c = 10.319$ (2) Å, $\beta = 96.89$ (2)°, $V = 1686.8$ (7) Å³, $Z = 4$, $D_x = 1.602$, $D_m = 1.60$ (2) Mg m⁻³, $\lambda(Mo K\alpha) = 0.71069$ Å, $\mu = 128$ mm⁻¹, $F(000) = 824$, $T = 295$ (1) K, final $R = 0.0410$, $wR = 0.0487$ for 2136 unique reflections and 165 parameters. Bond lengths and angles are normal. The configuration of the cation is *S,R* and the conformation is δ,δ,λ (or *R,S; \lambda,\delta,\delta*).

Introduction. We have undertaken a series of chemical and structural studies of the TcO^{3+} core attached to chelating ligands bound through N, O or S atoms. When made with the short-lived ^{99m}Tc isotope, these

compounds hold a twofold interest. They are of interest in their own right as potential imaging agents, in organs such as the brain (Lever, Burns, Kervitsky, Goldfarb, Woo, Wong, Epps, Kramer & Wagner, 1985) or as groups which can be added to a molecule which goes to a specific body site. In the latter case it is important that the added group is as far as possible from the recognition site of the biomolecule. These biomolecules can be simple (e.g. long-chain fatty acids) or complex (e.g. monoclonal antibodies). For the latter, obtaining direct evidence about the binding site of the metal is difficult, but information can be gathered by comparison of the extended X-ray absorption fine structure of the metal complex of the derivatized protein with that of model compounds for which detailed structural information is known. Binding of TcO^{3+} to ligands

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of the *N,N'*-bis(2-thiolatoethylene)ethylenediamine type activates the amine groups making them susceptible to loss of the protons and subsequent attack. In the present compound the H atoms of the amine groups have been exchanged with deuterons in heavy water. The chemistry of the system will be described by Epps, Kramer & Brune elsewhere.

Experimental. Density by suspension in dichloromethane–dibromomethane mixture. Crystal chosen for diffraction: parallelepiped, $0.30 \times 0.30 \times 0.50$ mm. Unit-cell parameters refined by least-squares fit of positional angles for 15 strong reflections, $19.5 < 2\theta < 24.6^\circ$, on Nicolet *P3* diffractometer, graphite-monochromated Mo $K\alpha$ radiation, 2521 reflections measured for $2\theta < 55^\circ$ at 295 K. Intensities $0 \leq h \leq 6$, $0 \leq k \leq 12$, $-11 \leq l \leq 11$ measured by θ – 2θ scan technique. Range of scan rates 4.9 to $29.3^\circ \text{ min}^{-1}$ in 2θ . Total background time to scan time was 1:1. Two standard reflections measured every 48 reflections (075, 1.5%; 1,14,1, 1.1%) showed no crystal or instrument instability. Zonal reflections averaged to give 2220 independent reflections, $R_{\text{int}} = 0.0216$, 2136 reflections with $I > 0$ used in structure solution and refinement. Lp corrections were made, but no corrections were made for absorption (absorption correction factors, A^* , 1.365–1.634 for maximum error in F_o or 4.5%). Structure solved by Patterson method. Anisotropic full-matrix least squares minimized $\sum w(|F_o| - |F_c|)^2$, $w = (\sigma_F^2 + 0.000197|F_o|^2)^{-1}$. Scale, positional and anisotropic temperature factors for non-H atoms varied, 165 parameters, H and D atoms on molecular cation included but not refined. D atoms on water molecule not found. The Cl and O atoms were refined in a disordered model. Initial refinement showed a partial occupancy of each atom on the two sites of almost exactly 0.5 so the value was fixed at 0.5. The positional parameters of Cl1 and O1 as well as Cl2 and O2 were tied at the same value. The thermal parameters of O1/O2 and Cl1/Cl2 were also tied. Final $R = 0.0410$, $wR = 0.0487$, $S = 2.174$. Refinement ended when $(\Delta/\sigma)_{\text{max}} = 0.20$. Final difference map revealed electron density difference max. 1.00, min. $-0.63 \text{ e } \text{\AA}^{-3}$. Six peaks in the range 1.00–0.48 $\text{e } \text{\AA}^{-3}$ were found near Cl1/O1 or Cl2/O2. They undoubtedly arise from the disorder, but attempts to refine the Cl and O atoms independently were unsuccessful. Scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B, pp. 99–101). Corrections for anomalous dispersion for Tc and S were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.3.1, pp. 149–150). Calculations employed *XTAL* (Stewart & Hall, 1983), *SHELX76* (Sheldrick, 1976), *CHEMX* (Davies, 1988) and *SNOOPI* (Davies, 1983) program systems on a VAX8650

Table 1. Atomic positional parameters ($\times 10^4$) and temperature factors ($\text{\AA}^2 \times 10^3$)

$$U_{\text{eq}} = 1/3(U_{11} + U_{22} + U_{33} + 2U_{13}\cos\gamma).$$

	x	y	z	U_{eq}
Tc1	2184.3 (6)	8595.5 (2)	7836.1 (4)	27.6
S1	516 (3)	8260.3 (5)	5984 (1)	42.7
S2	1519 (3)	7861.2 (5)	8817 (1)	42.9
N1	727 (6)	9272 (2)	7042 (4)	30
N2	955 (6)	8902 (2)	9509 (4)	31
C1	–393 (9)	8818 (2)	4989 (5)	36
C2	–1073 (9)	9202 (2)	5934 (5)	38
C3	70 (9)	9615 (2)	8082 (5)	38
C4	–735 (8)	9298 (2)	9137 (5)	35
C5	177 (10)	8540 (2)	10458 (5)	43
C6	1547 (9)	8064 (2)	10543 (5)	39
C11	–2392 (11)	8657 (2)	4041 (6)	56
C12	1429 (11)	9005 (3)	4228 (6)	60
C61	3868 (10)	8159 (2)	11745 (6)	51
C62	493 (12)	7566 (3)	11283 (7)	66
Cl1*	5673 (4)	15 (1)	3536 (2)	71
Cl2*	4466 (4)	9563 (1)	997 (2)	71
O1*	5673 (4)	15 (1)	3536 (2)	52
O2*	4466 (4)	9563 (1)	997 (2)	52
O3	4836 (6)	8654 (1)	7794 (4)	45

*Cl1/Cl2 and O1/O2 were disordered with 0.5 occupancy per atom.

computer. Atomic positional parameters and U_{eq} are given in Table 1.*

Discussion. The title compound was crystallized from weakly acid (DCI) heavy water and thus was deuterated at the N atoms. The deuteration is reflected in the infrared spectrum, which also shows the presence of lattice water which is only weakly hydrogen bonded to other groups. This is reflected in the sharpness of the $\nu_{\text{O-D}}$ absorptions, which occur at 2500 and 2600 cm^{-1} . We have seen this effect previously for $\nu_{\text{O-H}}$ vibrations of lattice water (Lock & Pilon, 1981). The $\nu_{\text{N-D}}$ vibration occurs as a broader band at $\sim 2400 \text{ cm}^{-1}$. Some doubt was cast on the presence of chlorine in the crystal under examination, since refinement proceeded smoothly with just O atoms at the positions where the disordered Cl/H₂O's were finally placed. Analysis of the bulk material agreed well with the title formulation, however, so the crystal was examined under an electron microscope by X-ray energy dispersive analysis. The results showed that the crystal contained chlorine, uniformly distributed throughout. It was only possible to include a Cl atom in the refinement if it was disordered with the water molecule, with a 50:50 distribution over the two sites. The molecular cation, A, is shown in Fig. 1 and interatomic distances are

* Lists of structure factors, anisotropic temperature factors, H-atom positions, bond lengths and angles involving H atoms and torsional angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53154 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Selected interatomic distances (Å) and angles (°) and hydrogen-bond geometry (°Å)

S1—C1	1.857 (5)	S2—C6	1.860 (5)
C1—C2	1.509 (7)	C6—C5	1.524 (8)
C2—N1	1.505 (6)	C5—N2	1.496 (7)
N1—C3	1.504 (6)	N2—C4	1.500 (7)
C1—C11	1.539 (8)	C6—C61	1.520 (8)
C1—C12	1.530 (8)	C6—C62	1.522 (8)
Tc—S1	2.245 (1)	Tc—S2	2.268 (2)
Tc—N1	2.137 (4)	Tc—N2	2.130 (4)
Tc—O	1.646 (4)	C3—C4	1.510 (8)
Tc—S1—C1	103.1 (2)	Tc—S2—C6	101.2 (2)
S1—C1—C2	106.1 (3)	S2—C6—C5	104.3 (4)
S1—C1—C11	107.0 (4)	S2—C6—C61	111.0 (4)
S1—C1—C12	110.8 (4)	S2—C6—C62	108.4 (4)
C11—C1—C12	110.2 (5)	C61—C6—C62	109.9 (5)
C11—C1—C2	109.7 (5)	C61—C6—C5	111.8 (5)
C12—C1—C2	112.8 (5)	C62—C6—C5	111.2 (5)
C1—C2—N1	109.8 (4)	C6—C5—N2	111.0 (4)
C2—N1—Tc	115.1 (3)	C5—N2—Tc	117.0 (3)
C2—N1—C3	112.4 (4)	C5—N2—C4	110.8 (4)
Tc—N1—C3	112.2 (3)	Tc—N2—C4	111.5 (3)
N1—C3—C4	108.2 (4)	N2—C4—C3	107.6 (4)
S1—Tc—N1	82.2 (1)	S2—Tc—N2	82.6 (1)
S1—Tc—N2	132.2 (1)	S2—Tc—N1	144.4 (1)
S1—Tc—O	111.7 (1)	S2—Tc—O	109.1 (1)
S1—Tc—S2	86.9 (1)	N1—Tc—N2	79.1 (2)
N1—Tc—O	106.4 (2)	N2—Tc—O	115.8 (2)
N1...Cl1*	3.037 (8)	N1—D1	0.95
D1...Cl1*	2.16	N1—D1...Cl1*	154
N2...Cl2*	3.060 (5)	N2—D2	0.98
D2...Cl2*	2.13	N2—D2...Cl2*	157
Cl1*...O2*	2.900 (3)		

*Cl1 and O1 are disordered and occupy the same positions as Cl2 and O2. No e.s.d.'s are given for parameters involving H atoms since these atoms were not refined.

given in Table 2. Bond lengths, except for the S—C bonds, which are significantly longer in the present compound [1.857 (5), 1.860 (5) vs 1.82 (1), 1.80 (1) Å], agree well with values obtained for a similar cation, *B*, which is methylated at the N atoms instead of C1 and C6 (Faggiani, Lock, Epps, Kramer & Brune, 1988). The configuration is again *S,R* (or *R,S*) so that, like the methyl groups in *B*, the H atoms point up from the base of the rough square pyramid about the Tc atom, in the same direction as the O atom. Some corresponding angles in *A* and *B* do differ significantly, but not by more than one or two degrees. The conformation of the cation *A* in Fig. 1 is δ, δ, λ (λ, λ, δ for the centrosymmetrically related cation), similar to *B*. A comparison of torsional angles shows reasonably good agreement with differences ranging from -22.1 (8) to 10.1 (8)°, with the moduli averaging 5.2° . The largest variations are associated with the bonds to C6 and to a much lesser extent C1, and are in the direction expected if C1 and C6 were rotated to move C61 and C12 away from O3. This means that C1 and C6 are further below the square pyramid (O3 is up) than in *B*. One might have expected a similar rotation of the N atoms in cation *B* to move the methyl groups away from the O atom, since methyl groups are bulkier than H atoms, but a

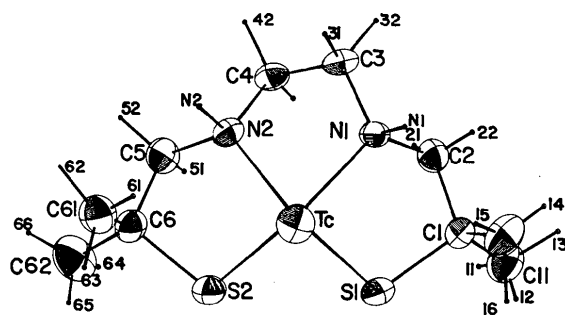
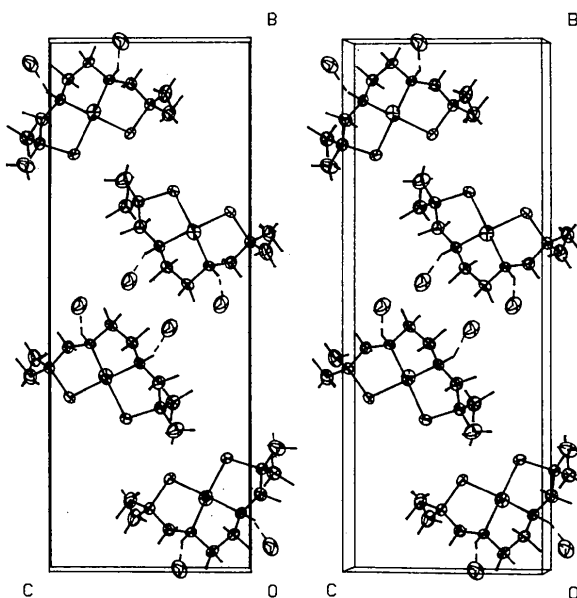


Fig. 1. The molecular cation, showing the atom numbering. H atoms are marked by affixes only, in smaller print.

Fig. 2. The packing within the unit cell; c^* and b are parallel to the bottom and sides of the page and the view is down a . Hydrogen bonds are indicated by broken lines.

comparison of torsional angles shows the reverse is the case, although the changes are not great [N1, range 1.1 (8)– 11.9 (8), av. 4.8° , N2, range 0.0 (8)– 11.5 (8), av. 3.5°].

The packing is shown in Fig. 2. Interactions are primarily van der Waals, but pairs of cations related by the inversion centre at $\frac{1}{2}, 0, 0$ (or $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) are bound together by two N1...Cl1/O1...Cl2/O2...N2 hydrogen-bonding chains.

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Structure of Aqua(ethylenediaminetetraacetato)ruthenium(III)

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Abstract. [Ru(C₁₀H₁₃N₂O₈)(H₂O)], $M_r = 408.31$, monoclinic, $P2_1/c$, $a = 8.415(2)$, $b = 8.831(1)$, $c = 17.633(3)$ Å, $\beta = 99.66(1)^\circ$, $V = 1291.8(4)$ Å³, $Z = 4$, $D_x = 2.10$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.70930$ Å, $\mu = 12.4$ cm⁻¹, $F(000) = 820$, room temperature, $R = 0.035$ for 3810 independent reflections [$I > 3\sigma(I)$]. The Ru is surrounded octahedrally by one O atom of water, and three O and two N atoms of the title ligand (Hedta).

Introduction. Recently the Ru^{III}-edta (edta: ethylenediaminetetraacetate) system has been discussed in relation to its catalytic activity (Taqi Khan, Shukla & Rao, 1989) and its reactivity in ligand substitution (Bajaj & van Eldik, 1988). In these circumstances, it is important to clarify the detailed structure of the Ru^{III}-edta complex. Based on the infrared spectrum, Mukaida, Okuno & Ishimori (1965) suggested that the Ru^{III}-(Hedta).5H₂O complex has a quinque-dentately coordinated edta ligand with a free carboxylic acid moiety. No X-ray studies of the Ru-edta complexes have been reported. Thus we report the crystal structure determination of [Ru(Hedta)(H₂O)].

Experimental. The title complex was prepared as follows: the crude powdery product of the Ru^{III}-edta complex was prepared according to the literature method (Mukaida, Okuno & Ishimori, 1965). The powder was dissolved in hot water (1 g in ca 60 cm³)

and the solution was kept at ambient temperature. Small yellow crystals appeared after 3–4 h. Crystals of a suitable size for X-ray analysis were obtained on growing for 2–3 days.

Yellow crystal 0.45 × 0.40 × 0.30 mm; Enraf-Nonius CAD-4 diffractometer, 50 kV and 26 mA; unit-cell dimensions by least-squares refinement from 25 reflections with $22 < 2\theta < 26^\circ$; ω - 2θ scan, scan rate varied from 1 to 5° min⁻¹ (in ω), scan width (0.8 + 0.350 tan θ)°; three intensity standards were monitored every 2 h of X-ray exposure time and these intensities remained constant within experimental error throughout the data collection; orientation (for the same three reflections) was monitored after every 200th scan; 3995 unique reflections, $2\theta \leq 60^\circ$ ($0 \leq h \leq 11$, $0 \leq k \leq 12$, $-24 \leq l \leq 24$); 3810 reflections with $I > 3\sigma(I)$ were used for structure determination; intensities were corrected for Lorentz and polarization; an empirical absorption correction based on a series of ψ scans was applied (max. and min. transmission factors 0.92 and 1.00). The Ru-, three O-, and N-atom positions were determined from direct methods and the other non-H-atom positions were determined from successive difference Fourier maps. No H atoms were included in the calculation. The structure refined by full-matrix least squares using anisotropic thermal parameters for non-H atoms; $R = 0.035$ and $wR = 0.047$, $w = 4F_o^2/\sigma^2(F_o)^2$, $\Delta_{\text{max}} = 0.03\sigma$; $|\Delta\rho|_{\text{max}}$ in final difference Fourier map = 1.14 e Å⁻³ (these highest peaks correspond to the calculated hydrogen positions but their positions

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