

Fig. 1. ORTEP drawing (Johnson, 1965) of the title molecule, with thermal ellipsoids at the 50% probability level.

while the O—U—Cp angles are less than 109° (Table 2). The extent of deviation of the structure from a regular tetrahedron is also shown by the distance of the U atom from the plane defined by the centres of the three Cp rings. If one assumes a tetrahedral geometry about the U atom and an average uranium to ring-centre distance of 2.463 Å, then the U atom should be located 0.821 Å above the plane. This distance here is 0.449 Å and measures the trigonal distortion from a tetrahedral geometry.

The phenyl ring and the Cp rings are planar with average deviations from their least-squares planes of 0.008 (11), 0.016 (13), 0.002 (13) and 0.011 (12) Å. The O atom lies in the phenyl plane and the U—O—C(16) angle is $159.4(5)^\circ$. The phenyl C—C distances and the Cp C—C distances average 1.39 (2) and 1.41 (2) Å, respectively, and the internal angles are 120 (1) and $108(1)^\circ$. The placement of the phenyl ring divides the Cp rings into two classes. Cp II and Cp III are non-parallel with the phenyl moiety [the angles are $60.9(4)$ and $74.5(4)^\circ$] while Cp I is nearly parallel to the phenyl moiety [$13.8(1.6)^\circ$]. In addition the angle at U from the Cp I centre to the oxygen is less than for the other two Cp rings. There are several short intramolecular contacts which may result from steric hindrance in the coordination sphere of uranium (Table 2c).

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Structural Characterization of the Ru^{III} Benzonitrile Complexes (Bu₄N)[RuCl₄(C₆H₅CN)₂] and [RuCl₃(C₆H₅CN)₃]

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Abstract. Tetrabutylammonium *trans*-bis-(benzonitrile)tetrachlororuthenate(III), C₁₂H₂₈N⁺·[RuCl₄(C₆H₅N)₂]⁻, *M_r* = 691.60, monoclinic, *P*2₁/*c*, *a* = 15.627 (2), *b* = 13.936 (2), *c* = 17.319 (1) Å, β = 113.66 (1)°, *V* = 3454.7 Å³, *Z* = 4, *D_x* = 1.330 Mg m⁻³, λ(Mo *K*α) = 0.71069 Å, μ = 0.78 mm⁻¹, *F*(000) = 1436, *T* = 298 K, *R* = 0.039 for 4478

observed reflections. There are two independent anions to the asymmetric unit, each with $\bar{1}$ symmetry. In one molecule Ru—Cl = 2.356 (2) and 2.348 (1) Å and Ru—N = 2.024 (3) Å; in the other Ru—Cl = 2.354 (1) and 2.356 (1) Å and Ru—N = 2.002 (3) Å. *mer*-Tris(benzonitrile)trichlororuthenium(III) hemibenzenonitrile solvate, [RuCl₃(C₆H₅N)₃].0.5C₆H₅N, *M_r* = 568.36, triclinic, *P* $\bar{1}$, *a* = 9.981 (5), *b* = 10.895 (5), *c* = 11.563 (5) Å, α = 80.86 (5), β = 87.60 (5), γ = 88.64 (5)°, *V* = 1240.2 Å³, *Z* = 2, *D_x* = 1.522 Mg m⁻³, λ(Mo *K*α) =

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0.71069 Å, $\mu = 0.96 \text{ mm}^{-1}$, $F(000) = 568$, $T = 298 \text{ K}$, $R = 0.050$ for 1892 observed reflections. Ru—Cl = 2.322 (3), 2.326 (4) and (*trans* to nitrile) 2.293 (3) Å; Ru—N = 2.011 (8), 2.009 (8) and (*trans* to Cl) 2.060 (9) Å. We conclude from these and related structures that packing forces rather than electronic π -back-bonding effects determine the orientation of the benzonitrile ligands.

Introduction. The two related complexes reported here are a subset of a larger family with the general formula $[\text{Ru}^{\text{III}}\text{X}_{6-n}(\text{RCN})_n]^{n-3}$ (Duff & Heath, 1990*b*). Our interest in these compounds is prompted by the identification of trends in their electrochemistry and electronic spectra (Duff & Heath, 1990*a*). Within these series, the $n = 2, 3$ and 4 compounds permit geometrical isomerism and the determination of their structures was undertaken to identify the isomers unambiguously. The intimate relationship between molecular symmetry and optical transitions, and the possible link with electrode potentials (Bursten, 1982), made the structural analysis of these complexes important. We are hoping to prepare single crystals of other members of the series and, in particular, to make direct comparisons of Ru^{II} and Ru^{III} forms having the same stoichiometry.

Experimental. $(\text{Bu}_4\text{N})[\text{RuCl}_4(\text{C}_6\text{H}_5\text{CN})_2]$ was prepared by stirring a suspension of K_3RuCl_6 in benzonitrile containing equimolar Bu_4NCl at room temperature until precipitation of KCl had ceased. The title compound was recovered from the filtrate in 80% yield by precipitation with diethyl ether. Single crystals were grown from a methylene chloride/diethyl ether solution at 278 K. Orange crystal of size $0.24 \times 0.16 \times 0.39 \text{ mm}$. Philips PW1100/20 diffractometer, graphite monochromator. Lattice parameters from least-squares analysis of setting angles of 25 reflections $39 < 2\theta < 45^\circ$, $\lambda(K\alpha_1) = 0.70930 \text{ \AA}$. θ - 2θ scans of $(1.6 + 0.692 \tan\theta)^\circ$ in 2θ at 4° min^{-1} with 6 s backgrounds on each side of every scan, $2\theta_{\text{max}} = 55^\circ$, $h = 19 \rightarrow 18$, $k = 0 \rightarrow 18$, $l = 0 \rightarrow 22$, three check reflections measured at regular intervals showed no systematic variations in intensity, 7983 unique reflections, 3505 with $I < 3\sigma(I)$ regarded as unobserved, absorption correction ($A^* = 1.21$ – 1.12). Structure solution by Patterson synthesis, ΔF synthesis and full-matrix least-squares refinement with anisotropic displacement factors for all non-H atoms [except for the phenyl ring C(22)–C(27) which was disordered over two orientations and so was modelled by two planar rings which were refined as rigid bodies with atoms of half occupancy and individual isotropic displacement factors]. H atoms positioned geometrically and not refined. Refinement on F , 311 parameters, to $R = 0.039$, $wR = 0.048$, $S = 1.47$, weighting scheme $w = [\sigma^2(F) +$

Table 1. Atomic coordinates and isotropic displacement parameters (\AA^2) for the non-H atoms in $(\text{Bu}_4\text{N})[\text{RuCl}_4(\text{C}_6\text{H}_5\text{CN})_2]$

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}/U
Ru(1)	0	0	0	0
Cl(11)	0.04464 (9)	-0.03272 (9)	-0.11207 (7)	0.0481 (2)
Cl(12)	-0.05185 (9)	0.15241 (8)	-0.05751 (8)	0.0674 (6)
N(1)	0.1283 (3)	0.0562 (3)	0.0655 (2)	0.0686 (7)
C(11)	0.1995 (3)	0.0892 (3)	0.0978 (3)	0.057 (2)
C(12)	0.2914 (3)	0.1320 (3)	0.1353 (2)	0.054 (2)
C(13)	0.3102 (4)	0.2151 (4)	0.1024 (3)	0.049 (2)
C(14)	0.3981 (5)	0.2532 (4)	0.1348 (4)	0.071 (3)
C(15)	0.4678 (4)	0.2076 (5)	0.1987 (4)	0.086 (4)
C(16)	0.4501 (3)	0.1256 (4)	0.2331 (3)	0.087 (4)
C(17)	0.3617 (3)	0.0866 (3)	0.2022 (3)	0.075 (3)
Ru(2)	0.5	0	0.5	0.055 (2)
Cl(21)	0.38245 (7)	-0.01149 (8)	0.55205 (7)	0.0386 (2)
Cl(22)	0.59540 (7)	0.07709 (8)	0.62638 (6)	0.0536 (5)
N(2)	0.4521 (2)	0.1297 (2)	0.4525 (2)	0.0537 (5)
C(21)	0.4285 (3)	0.2054 (3)	0.4299 (3)	0.047 (2)
C(22A)*	0.4078 (6)	0.3033 (4)	0.4065 (5)	0.050 (2)
C(23A)*	0.4322 (5)	0.3743 (5)	0.4664 (3)	0.054 (1)†
C(24A)*	0.4169 (4)	0.4687 (5)	0.4423 (4)	0.091 (2)†
C(25A)*	0.3772 (4)	0.4922 (4)	0.3583 (4)	0.113 (3)†
C(26A)*	0.3528 (4)	0.4212 (5)	0.2984 (3)	0.100 (3)†
C(27A)*	0.3681 (5)	0.3268 (4)	0.3225 (4)	0.098 (2)†
C(22B)*	0.3948 (9)	0.3021 (6)	0.3955 (7)	0.068 (2)†
C(23B)*	0.3449 (9)	0.3549 (8)	0.4300 (6)	0.054 (1)†
C(24B)*	0.3154 (7)	0.4457 (8)	0.4008 (6)	0.091 (2)†
C(25B)*	0.3359 (7)	0.4837 (6)	0.3371 (6)	0.113 (3)†
C(26B)*	0.3858 (7)	0.4309 (8)	0.3026 (6)	0.100 (3)†
C(27B)*	0.4153 (8)	0.3401 (8)	0.3318 (7)	0.098 (2)†
N(3)	0.8658 (2)	0.1797 (2)	0.6529 (2)	0.068 (2)†
C(31)	0.8608 (3)	0.0830 (3)	0.6925 (3)	0.045 (2)
C(32)	0.8528 (3)	-0.0035 (3)	0.6386 (3)	0.055 (2)
C(33)	0.8340 (4)	-0.0935 (4)	0.6800 (3)	0.065 (2)
C(34)	0.8234 (5)	-0.1800 (4)	0.6258 (4)	0.090 (3)
C(41)	0.7727 (3)	0.1964 (3)	0.5795 (2)	0.105 (4)
C(42)	0.7616 (3)	0.2913 (3)	0.5346 (3)	0.046 (2)
C(43)	0.6635 (3)	0.2984 (3)	0.4659 (3)	0.053 (2)
C(44)	0.6539 (4)	0.3803 (4)	0.4063 (4)	0.065 (3)
C(51)	0.8861 (3)	0.2575 (3)	0.7192 (3)	0.094 (4)
C(52)	0.8107 (3)	0.2752 (3)	0.7514 (3)	0.052 (2)
C(53)	0.8385 (4)	0.3591 (3)	0.8127 (3)	0.058 (2)
C(54)	0.7722 (5)	0.3721 (4)	0.8561 (4)	0.071 (3)
C(61)	0.9419 (3)	0.1815 (3)	0.6195 (3)	0.096 (4)
C(62)	1.0386 (3)	0.1537 (4)	0.6808 (3)	0.056 (2)
C(63)	1.1084 (4)	0.1671 (5)	0.6418 (4)	0.075 (3)
C(64)	1.0930 (5)	0.1102 (5)	0.5670 (5)	0.087 (4)

* Atoms C(2*n*A) have occupancy 0.614 (4) and atoms C(2*n*B) have occupancy 0.386 (4).

† Atoms refined isotropically.

$(0.0004)F^2]^{-1}$, max. $\Delta/\sigma = 0.1$, max. and min. heights in final $\Delta\rho$ map 0.68 and -0.89 e \AA^{-3} respectively (major features close to Ru atom or atoms of disordered phenyl group). Final parameters for the non-H atoms are given in Table 1 while selected bond distances are given in Table 3. The numbering scheme used is shown in Fig. 1.

$[\text{RuCl}_3(\text{C}_6\text{H}_5\text{CN})_3] \cdot 0.5(\text{C}_6\text{H}_5\text{CN})$ was prepared by modification (Duff & Heath, 1990*b*) of the procedure of Dehand & Rose (1979). $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ was heated in benzonitrile at 353 K for 45 min. Upon cooling and the addition of diethyl ether the compound was isolated in 80% yield. In solution the compound is prone to dimerization forming $[\text{Ru}_2\text{Cl}_6(\text{C}_6\text{H}_5\text{CN})_4]$, however single crystals were grown from a benzonitrile/methylene chloride/diethyl ether solution at

room temperature. Orange-red crystal of size $0.03 \times 0.20 \times 0.24$ mm. Philips PW1100/20 diffractometer, graphite monochromator. Lattice parameters from least-squares analysis of setting angles of 24 reflections $37 < 2\theta < 43^\circ$, $\lambda(K\alpha_1) = 0.70930$ Å. θ - 2θ scans of $(1.8 + 0.692 \tan \theta)^\circ$ in 2θ at 6° min^{-1} with 5 s backgrounds on each side of every scan, $2\theta_{\text{max}} = 45^\circ$, $h - 10 \rightarrow 10$, $k - 11 \rightarrow 11$, $l 0 \rightarrow 13$, three check reflections showed no systematic variations in intensity, 4357 unique reflections, 2465 with $I < 3\sigma(I)$ regarded as unobserved, absorption correction ($A^* = 1.18$ – 1.03). Structure solution by Patterson synthesis, ΔF synthesis and full-matrix least-squares refinement with anisotropic displacement factors for all non-H atoms (except for the solvate molecule which was refined as a rigid body with atoms of half occupancy and individual isotropic displacement factors). H atoms positioned geometrically and not refined (solvate H atoms not included). Refinement on F , 264 parameters, to $R = 0.050$, $wR = 0.049$, $S = 1.24$, weighting scheme $w = [\sigma^2(F) + (0.0004)F^2]^{-1}$, max. $\Delta/\sigma = 0.23$, max. and min. heights in final $\Delta\rho$ map 0.49 and $-0.49 e \text{ \AA}^{-3}$, respectively (major features close to Ru atom or atoms of solvate). Final parameters for the non-H atoms are given in Table 2 while selected bond distances are given in Table 4.*

* Figures of the second anion and the cation of $(Bu_4N)[RuCl_4(C_6H_5CN)_2]$, lists of H-atom coordinates, anisotropic displacement parameters, additional interatomic distances and angles, torsion angles, least-squares planes and structure-factor amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53181 (81 pp.). Copies may be obtained through the Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

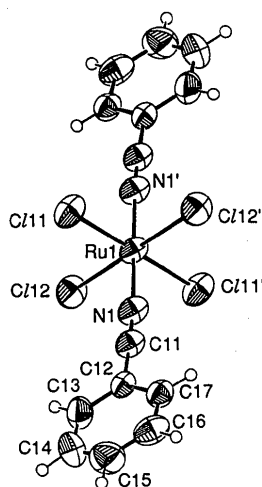


Fig. 1. A view of one of the independent $[RuCl_4(C_6H_5CN)_2]^-$ anions showing the labelling of the non-H atoms. Thermal ellipsoids are shown at 50% probability levels except for H atoms which are drawn as small circles.

Table 2. Atomic coordinates and isotropic displacement parameters (\AA^2) for the non-H atoms in $[RuCl_3(C_6H_5CN)_3] \cdot 0.5(C_6H_5CN)$

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}/U
Ru	0.18013 (11)	0.34532 (8)	0.16346 (8)	0.0454 (6)
Cl(1)	-0.0326 (3)	0.2984 (2)	0.1112 (2)	0.065 (2)
Cl(2)	0.1284 (3)	0.2727 (3)	0.3570 (2)	0.075 (2)
Cl(3)	0.3967 (3)	0.3978 (3)	0.2015 (3)	0.078 (3)
N(1)	0.1157 (8)	0.5148 (7)	0.1916 (7)	0.050 (6)
C(1)	0.082 (1)	0.610 (1)	0.2109 (8)	0.052 (8)
C(11)	0.049 (1)	0.7302 (8)	0.244 (1)	0.047 (8)
C(12)	0.054 (1)	0.747 (1)	0.357 (1)	0.08 (1)
C(13)	0.031 (1)	0.868 (1)	0.381 (1)	0.09 (1)
C(14)	-0.001 (1)	0.963 (1)	0.293 (1)	0.08 (1)
C(15)	-0.014 (1)	0.943 (1)	0.182 (1)	0.07 (1)
C(16)	0.013 (1)	0.826 (1)	0.1540 (9)	0.056 (8)
N(2)	0.2241 (9)	0.4039 (8)	-0.0120 (8)	0.057 (7)
C(2)	0.244 (1)	0.428 (1)	-0.109 (1)	0.063 (9)
C(21)	0.269 (1)	0.448 (1)	-0.235 (1)	0.06 (1)
C(22)	0.274 (1)	0.568 (1)	-0.296 (1)	0.09 (1)
C(23)	0.295 (2)	0.582 (2)	-0.414 (2)	0.12 (2)
C(24)	0.316 (2)	0.484 (2)	-0.470 (1)	0.12 (2)
C(25)	0.314 (2)	0.368 (2)	-0.411 (2)	0.12 (2)
C(26)	0.291 (1)	0.349 (1)	-0.290 (1)	0.09 (1)
N(3)	0.2483 (9)	0.1761 (7)	0.1385 (7)	0.060 (7)
C(3)	0.285 (1)	0.0821 (9)	0.1231 (9)	0.058 (9)
C(31)	0.331 (1)	-0.042 (1)	0.105 (1)	0.058 (9)
C(32)	0.337 (1)	-0.066 (1)	-0.007 (1)	0.08 (1)
C(33)	0.377 (1)	-0.185 (1)	-0.027 (1)	0.09 (1)
C(34)	0.406 (1)	-0.274 (1)	0.065 (2)	0.11 (2)
C(35)	0.398 (1)	-0.249 (1)	-0.175 (1)	0.10 (1)
C(36)	0.364 (1)	-0.130 (1)	0.199 (1)	0.08 (1)
C(91)*	0.4698 (5)	-0.0156 (5)	0.5347 (2)	0.11 (1)
C(92)*	0.441 (2)	0.0818 (8)	0.4445 (8)	0.11 (1)
C(93)*	0.542 (3)	0.130 (1)	0.3637 (8)	0.14 (1)
C(94)*	0.672 (2)	0.080 (3)	0.373 (1)	0.16 (2)
C(95)*	0.7017 (3)	-0.017 (3)	0.463 (2)	0.16 (1)
C(96)*	0.600 (1)	-0.065 (1)	0.544 (1)	0.10 (1)
N(9)*	0.284 (3)	-0.104 (4)	0.683 (2)	0.31 (3)
C(9)*	0.365 (2)	-0.065 (2)	0.618 (1)	0.22 (3)

* Atoms C(91)–C(9) refined as a rigid body with occupancy 0.5 and isotropic displacement factors for each atom.

The numbering scheme used is shown in Fig. 2 and a stereoscopic view of the unit cell is given as Fig. 3.

Atomic scattering factors for neutral atoms and real and imaginary dispersion terms from *International Tables for X-ray Crystallography* (1974, Vol. IV). Data reduction and refinement computations performed with *XTAL2.4* and *XTAL2.6* (Hall & Stewart, 1988, 1989).

Discussion. The $[RuCl_4(C_6H_5CN)_2]^-$ compound is confirmed to have mutually *trans* nitrile ligands as suggested by its physical properties (Duff & Heath, 1990b). Similarly, a meridional geometry is confirmed for $RuCl_3(C_6H_5CN)_3$, so that it can be formally derived by replacing a specific chloride $[Cl(2)]$ by the additional nitrile ligand.

Disposition of the nitrile ligands. As the $-C\equiv N-$ moiety has axial symmetry, the phenyl substituent of benzonitrile is, in principle, free to rotate. However if ketene-like character is induced by coordination to a π -back-bonding metal ion this may no longer be so (Eysel, Guggolz, Kopp & Ziegler, 1983). In $[RuCl_4(C_6H_5CN)_2]^-$ the two C_6H_5CN ligands lie

Table 3. Selected interatomic distances (Å) and angles (°) in (Bu₄N)[RuCl₄(C₆H₅CN)₂]

Ru(1)—Cl(11)	2.3556 (15)	Ru(2)—Cl(21)	2.3541 (14)
Ru(1)—Cl(12)	2.3478 (12)	Ru(2)—Cl(22)	2.3556 (10)
Ru(1)—N(1)	2.024 (3)	Ru(2)—N(2)	2.002 (3)
N(1)—C(11)	1.124 (6)	N(2)—C(21)	1.135 (5)
C(11)—C(12)	1.447 (6)	C(21)—C(22A)	1.423 (7)
		C(21)—C(22B)	1.482 (10)
Cl(11)—Ru(1)—Cl(12)	89.51 (5)	Cl(21)—Ru(2)—Cl(22)	88.59 (4)
Cl(11)—Ru(1)—N(1)	88.98 (13)	Cl(21)—Ru(2)—N(2)	89.88 (12)
Cl(12)—Ru(1)—N(1)	89.03 (10)	Cl(22)—Ru(2)—N(2)	87.87 (9)
Ru(1)—N(1)—C(11)	176.3 (4)	Ru(2)—N(2)—C(21)	176.0 (3)
N(1)—C(11)—C(12)	177.1 (5)	N(2)—C(21)—C(22A)	174.5 (5)
		N(2)—C(21)—C(22B)	176.7 (5)

Table 4. Selected interatomic distances (Å) and angles (°) in [RuCl₃(C₆H₅CN)₃].0.5(C₆H₅CN)

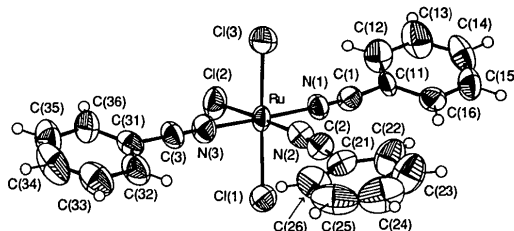
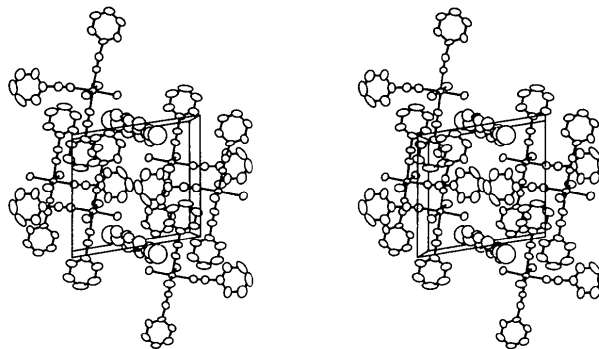
Ru—Cl(1)	2.322 (3)	Ru—N(1)	2.011 (8)
Ru—Cl(2)	2.293 (3)	Ru—N(2)	2.060 (9)
Ru—Cl(3)	2.326 (4)	Ru—N(3)	2.009 (8)
N(1)—C(1)	1.14 (1)	C(1)—C(11)	1.44 (1)
N(2)—C(2)	1.12 (2)	C(2)—C(21)	1.45 (2)
N(3)—C(3)	1.12 (1)	C(3)—C(31)	1.46 (2)
Cl(1)—Ru—Cl(2)	91.0 (1)	Cl(1)—Ru—Cl(3)	175.8 (1)
Cl(1)—Ru—N(1)	91.0 (3)	Cl(1)—Ru—N(2)	87.6 (3)
Cl(1)—Ru—N(3)	90.4 (3)	Cl(2)—Ru—Cl(3)	93.1 (1)
Cl(2)—Ru—N(1)	88.3 (2)	Cl(2)—Ru—N(2)	177.7 (3)
Cl(2)—Ru—N(3)	91.0 (2)	Cl(3)—Ru—N(1)	89.1 (3)
Cl(3)—Ru—N(2)	88.3 (3)	Cl(3)—Ru—N(3)	89.6 (3)
N(1)—Ru—N(2)	93.5 (3)	N(1)—Ru—N(3)	178.5 (3)
N(2)—Ru—N(3)	87.2 (3)	Ru—N(1)—C(1)	177.5 (8)
N(1)—C(1)—C(11)	175 (1)	Ru—N(2)—C(2)	174.8 (9)
N(2)—C(2)—C(21)	176 (1)	Ru—N(3)—C(3)	178.9 (9)
N(3)—C(3)—C(31)	179 (1)		

nearly perpendicular to the RuCl₄ plane. The phenyl rings are strictly parallel to each other (maintaining the centrosymmetry of the molecule) and nearly coplanar due to the approximate linearity of the —CN—Ru—NC— moiety. They are rotated 30° from eclipsing a *trans* Cl Ru Cl axis, where 45° represents the maximum displacement. This rotation need not in itself diminish long range Ru *dπ*/C₆H₅CN *pπ* conjugation because of the overall electronic symmetry of the metal ion, (*d_{xz}*)²(*d_{yz}*)²(*d_{xy}*)¹. However, if extended *π*-back-bonding effects were dictating mutual ligand alignment then, clearly, the *trans*-nitrile ligands should lie orthogonal to each other (avoiding competition for the same *d*-electron density) rather than parallel as is observed. We therefore believe that normal packing forces determine the alignment of the phenyl rings.

In the related RuCl₃(C₆H₅CN)₃ structure, the pair of *trans* nitrile ligands retain a similar disposition to that described above, but with less rotation. All three C₆H₅CN phenyl rings lie close to the plane defined by the RuCl(2)N(1)N(2)N(3) unit. Similar coplanarity of *cis* benzonitrile phenyl rings is observed in Ru(CO)₂(C₆H₅CN)₂Cl₂ (Daran, Jeannin & Rigault, 1984) and VOCl₃(C₆H₅CN)₂ (Daran, Gourdon & Jeannin, 1980). Each of these complexes possesses a

pair of *trans* chlorides and the V^V structure is related to the Ru^{II} structure by replacement of the *cis* CO ligands by O²⁻ and a further Cl⁻. In both cases, the orientation of the benzonitrile ligands has been attributed to overlap between phenyl ring *pπ*, nitrile *pπ* and Ru *dπ* orbitals, without regard to the contrasting electronic properties of the *trans* ligands (2 × CO vs O²⁻, Cl⁻). Since the formal *d*-orbital occupation of V^V is *d*⁰, in that case at least *dπ*-back-bonding effects are unlikely to be relevant. In our view these two structures, which are so chemically dissimilar, provide persuasive evidence that inter- and intramolecular packing forces control the disposition of the benzonitrile ligands. As described above, our own observations on [RuCl₄(C₆H₅CN)₂]⁻ and RuCl₃(C₆H₅CN)₃ lead to the same conclusion. It should be noted, however, that in both *cis* and *trans* Pt(C₆H₅CN)₂Cl₂ (Eysel *et al.*, 1983) the observed orientations of the benzonitrile ligands are apparently optimal for conjugation, whatever the underlying cause.

In all the cited structures, the benzonitrile ligands deviate slightly from linearity, being bent at both the nitrogen and the nitrile carbon (average 176°). The benzonitrile ligands in [RuCl₄(C₆H₅CN)₂]⁻ are bent in opposite directions, creating a centre of inversion.

Fig. 2. The [RuCl₃(C₆H₅CN)₃] molecule showing the labelling of the non-H atoms. Thermal ellipsoids are shown at 50% probability levels except for H atoms which are drawn as small circles.Fig. 3. Unit-cell contents (H atoms deleted) for [RuCl₃(C₆H₅CN)₃].0.5(C₆H₅CN), projected down the *a* axis.

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*; λ,δ,δ).

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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