Kobus, H. J., Stoilovic, M. & Warrener, R. N. (1983). *Forens. Sci. Int.* **22**, 161–170.
Lennard, C. J., Margot, P. A., Sterns, M. & Warrener, R. N. (1987). *J. Forens. Sci.* **32**, 597–605.
Menzel, E. R., Bartsch, R. A. & Hallman, J. L. (1990). *J. Forens. Sci.* **35**, 25–34.
Stoilovic, M., Kobus, H. J., Warrener, R. N. & Margot, P. A. (1986). *J. Forens. Sci.* **31**, 432–445.

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Tetraethylammonium Salt of *trans*-Bis(acetonitrile)tetrachlororuthenate(III), a Notable Optical Chromophore

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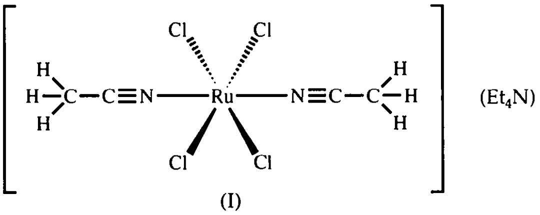
Abstract

In accord with its optical and electrochemical properties, the complex anion of the title compound, *trans*-$[(C_2H_5)_4N][RuCl_4(C_2H_3N)_2]$, displays almost perfect tetragonal symmetry, with *trans*-linear MeCN coordination.

Comment

Tetraethylammonium *trans*-bis(acetonitrile)tetrachlororuthenate(III), (I), is an important member of an extended substitutional series with the general formula $[Ru^{III}Cl_{6-n}(MeCN)_n]^{n-3}$ (n = 1–6) under examination in our laboratory. This family shows very orderly progressions in metal-centered electrode potentials and charge-transfer spectra as a function of stoichiometry and structure, and so provides a means of testing conflicting electronic theories of ligand additivity (Duff & Heath, 1991*a*). We described recently the molecular geometry of the benzonitrile complexes *trans*-$[RuCl_4(PhCN)_2]^-$ and *mer*-$[RuCl_3(PhCN)_3]$ (Duff, Heath & Willis, 1990) and now extend our studies to include the corresponding acetonitrile compound *trans*-$[RuCl_4(MeCN)_2]^-$, (I).



(I)

This compound constitutes a most instructive tetragonal MX_4L_2 chromophore, due in part to the exceptional redox inertness and UV-transparency of acetonitrile ligands (even when compared with PhCN). The UV/visible spectrum of (I) reveals a well defined set of charge-transfer bands spanning Cl(π/σ) to Ru(d_{xy}) and to Ru($d_{x^2-y^2}$) (Duff & Heath, 1991*b*). There is also the prospect of locating the direct tetragonal crystal-field transition (d_{xz}, $d_{yz} \rightarrow d_{xy}$) which is known only in the 5*d* osmium analogue (Heath & Humphrey, 1991). The present structure determination opens the way for detailed single-crystal optical and EPR measurements to examine these assignments.

The X-ray analysis of the title compound reveals discrete well defined $[RuCl_4(MeCN)_2]^-$ anions and $[Et_4N]^+$ cations, with both ions occupying special positions. As expected, the pertinent bond lengths observed for the anion in (I) resemble those in the PhCN analogue, where the mean measured values are Ru—Cl 2.353, Ru—N 2.013 and N—C 1.130 Å and Ru—N—C 176.1°. The inner coordination sphere closely approximates true tetragonal geometry though only a centre of symmetry is crystallographically imposed on the molecule. Thus the Ru—Cl(1) and Ru—Cl(2) bonds are experimentally indistinguishable, and the *cis*-Cl—Ru—Cl and Cl—Ru—N angles approach 90°, within 1.0 and 1.5°, respectively. The MeCN moiety is virtually linear within experimental error [N—C—C 179.1 (5)°] and tilted only slightly (but measurably) from collinearity with Ru [Ru—N—C 177.0 (4)°].

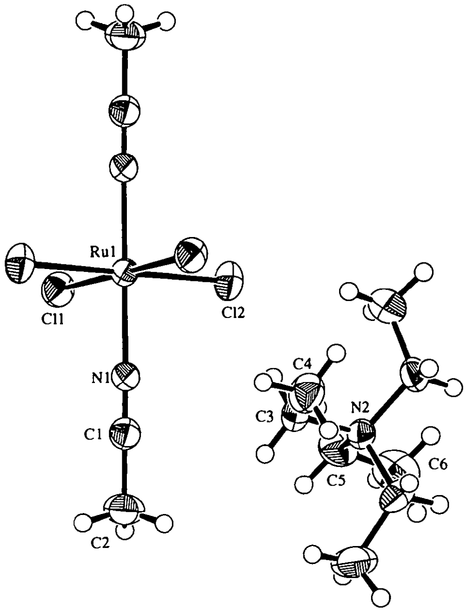


Fig. 1. View of (I) showing the labelling of all unique non-H atoms. Displacement ellipsoids are shown at 50% probability levels. H atoms are drawn as circles of arbitrary radii.

The crystal symmetry ensures that the four $[RuCl_4(MeCN)_2]^-$ sites in the present unit cell are indistinguishable, unlike the lattice structure of the PhCN analogue which contains two independent molecules (Duff, Heath & Willis, 1990). Thus, $[Et_4N][RuCl_4(MeCN)_2]$ with all sites equivalent is well favoured for single-crystal spectroscopic and magnetic studies. X-ray structure determinations of monomeric Ru^{III}/MeCN complexes are not common, with only one prior to 1990 cited elsewhere (Duff, Heath & Willis, 1990). One further example, comparable in its simplicity to the present case, is sterically encumbered five-coordinate $[Ru(MeCN)_2(S\text{-}Ar)_3]$, where Ar = 2,4,6-triisopropylphenyl (Satsangee, Hain, Cooper & Koch, 1992).

Experimental

Crystals of the tetraethylammonium salt of *trans*-bis(acetonitrile)tetrachlororuthenium(III), prepared as in the literature (Duff & Heath, 1991*b*), were grown by vapour diffusion from a $CH_3CN/(C_2H_5)_2O$ mixture.

Crystal data

$(C_8H_{20}N)[RuCl_4(C_2H_3N)_2]$
$M_r = 455.24$
Monoclinic
$C2/c$
$a = 19.582\,(2)$ Å
$b = 7.668\,(2)$ Å
$c = 14.138\,(2)$ Å
$\beta = 111.229\,(9)°$
$V = 1978.9\,(6)$ Å^3
$Z = 4$
$D_x = 1.528$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 26.2\text{–}33.2°$
$\mu = 11.342$ mm^{-1}
$T = 296$ K
Prism
0.10 × 0.08 × 0.08 mm
Yellow

Data collection

Rigaku AFC-6*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: azimuthal ψ scan (North, Phillips & Mathews, 1968)
$T_{min} = 0.908$, $T_{max} = 0.996$
1654 measured reflections
1598 independent reflections

1173 observed reflections $[I > 3\sigma(I)]$
$R_{int} = 0.025$
$\theta_{max} = 60.02°$
$h = 0 \rightarrow 22$
$k = 0 \rightarrow 8$
$l = -15 \rightarrow 14$
3 standard reflections monitored every 150 reflections intensity decay: 0.75%

Refinement

Refinement on F
$R = 0.025$
$wR = 0.022$
$S = 1.73$
1173 reflections
93 parameters
H-atom parameters not refined
$w = 4F_o^2/[\sigma^2(F_o^2) + (0.001F_o^2)^2]$

$(\Delta/\sigma)_{max} = 0.005$
$\Delta\rho_{max} = 0.27$ e Å^{-3}
$\Delta\rho_{min} = -0.39$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Ru(1)	1/4	1/4	0	0.0313 (2)
Cl(1)	0.34266 (6)	0.1188 (1)	0.13810 (8)	0.0444 (4)
Cl(2)	0.15891 (6)	0.1185 (2)	0.04823 (8)	0.0469 (5)
N(1)	0.2504 (2)	0.0380 (4)	−0.0847 (3)	0.037 (2)
N(2)	0	−0.1159 (6)	−1/4	0.037 (2)
C(1)	0.2525 (2)	−0.0809 (6)	−0.1271 (3)	0.040 (2)
C(2)	0.2549 (3)	−0.2377 (6)	−0.1851 (3)	0.055 (2)
C(3)	0.0570 (2)	−0.0037 (6)	−0.2706 (3)	0.044 (2)
C(4)	0.0265 (3)	0.1265 (7)	−0.3562 (4)	0.057 (2)
C(5)	0.0417 (2)	−0.2261 (6)	−0.1582 (3)	0.052 (2)
C(6)	−0.0046 (3)	−0.3538 (7)	−0.1251 (4)	0.070 (3)

Table 2. *Selected geometric parameters* (Å, °)

Ru(1)—Cl(1)	2.356 (1)	N(1)—C(1)	1.100 (5)
Ru(1)—Cl(2)	2.355 (1)	C(1)—C(2)	1.465 (6)
Ru(1)—N(1)	2.020 (4)		
Cl(1)—Ru(1)—Cl(2)	90.80 (4)	Ru(1)—N(1)—C(1)	177.0 (4)
Cl(1)—Ru(1)—N(1)	88.9 (1)	N(1)—C(1)—C(2)	179.1 (5)
Cl(2)—Ru(1)—N(1)	89.6 (1)		

The θ scan width used was $(1.20 + 0.3\tan\theta)°$ at a speed of 8.0° min^{-1} (in ω). The weak reflections were rescanned a maximum of four times and the counts accumulated to ensure good counting statistics. Stationary background counts were made on each side of the reflection with a 2:1 ratio of peak to background counting time. H atoms were located from a difference map and fixed at ideal position with $U_{iso} = 1.2U_{eq}(C)$. The structure was solved by direct methods (Sheldrick, 1985) and expanded using Fourier techniques (*DIRDIF*; Beurskens *et al.*, 1992).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1993). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: TA1023). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Beurskens, P. T., Admiraal, G., Beurskens, G., Bosman, W. P., Garcia-Grande, S., Gould, R. O., Smits, J. M. M. & Smykalla, C. (1992). *DIRDIF*92. *The DIRDIF Program System*. Technical Report. Crystallography Laboratory, Univ. of Nijmegen, The Netherlands.

Duff, C. M. & Heath, G. A. (1991*a*). *Inorg. Chem.* **30**, 2528–2535.

Duff, C. M. & Heath, G. A. (1991*b*). *J. Chem. Soc. Dalton Trans.* pp. 2401–2411.

Duff, C. M., Heath, G. A. & Willis, A. C. (1990). *Acta Cryst.* C**46**, 2321–2324.

Heath, G. A. & Humphrey, D. G. (1991). *J. Chem. Soc. Chem. Commun.* pp. 1668–1671.

Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1993). *TEXSAN. Single Crystal Structure Analysis Software*. Version 1.6c. MSC, The Woodlands, TX 77381, USA.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Satsangee, S. P., Hain, J. H. Jr, Cooper, P. T. & Koch, S. A. (1992). *Inorg. Chem.* **31**, 5160.
Sheldrick, G. M. (1985). *SHELXS86. Crystallographic Computing* 3, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 175–189. Oxford Univ. Press.

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(Acetonitrile)-*trans*-dichloro-*mer*-tris[(dimethyl)phenylphosphine]osmium(III); the Kinetically Controlled Electrogenerated Isomer

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Abstract

The electrosynthesized compound, *trans-mer*-$[OsCl_2(C_2H_3N)(C_8H_{11}P)_3]$, contains a nearly linear MeC≡N—Os linkage [Os(1)—N(1)—C(1) 179(1)°] and the phenyl substituents on neighbouring phosphines are specifically oriented about the nitrile ligand.

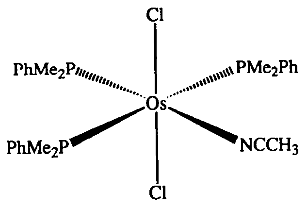
Comment

trans-mer-$[Os^{II}Cl_2(PMe_2Ph)_3(MeCN)]$, (I), is formally an MeCN-substituted analogue of the more familiar complex *trans*-$[Os^{II}Cl_2(PMe_2Ph)_4]$, but is actually isolated in a redox-induced halide displacement reaction:

$$mer\text{-}[Os^{III}Cl_3(PR_3)_3] \xrightarrow{+1e^-} Cl^- + \underset{\text{very reactive}}{\{Os^{II}Cl_2(PR_3)_3\}} \xrightarrow{+MeCN} \underset{\text{(I)}}{[OsCl_2(PR_3)_3(MeCN)]}$$

Such electrosynthetic procedures have been elevated to the status of 'rational pathways to osmium(II) complexes' (Coombe, Heath, Stephenson, Whitelock & Yellowlees, 1985).

All potential isomers of (I) (*trans-mer*, *cis-mer* and *cis-fac*) possess inequivalent phosphine ligands in the ratio 1:2, as required by the ^{31}P NMR data, and this is the first X-ray confirmation of the *trans-mer* assignment for the kinetically controlled product. On standing in solution, (I) relaxes to the presumed *cis-mer* isomer.



(I)

The pertinent bond lengths and angles in (I) are unexceptional, and compare well with, for example, *trans*-$[OsCl_2(dppe)_2]$ (Levason, Champness & Webster, 1993), with Os—Cl = 2.434 Å, and Os—P(mean) = 2.36 Å. A greater *trans*-influence of PMe_2Ph compared with MeCN on Os—P bond lengths is also evident [the difference between Os—P(1,3) and Os—P(2) being approximately 0.05 Å].

The *trans*-MeCN—Os—P moiety is essentially linear and comparable to the MeCN—Ru—NCMe fragment recently described for *trans*-$[RuCl_4(MeCN)_2]^-$ (Gheller, Heath & Hockless, 1995).

The phenyl substituents on neighbouring phosphines seem specifically oriented about the nitrile ligand. Viewed down the P(1)–P(3) axis, these rings are eclipsed (and accidentally perpendicular to this axis) and are seen to partially enclose the MeCN group, with both phosphines tilted slightly in this direction.

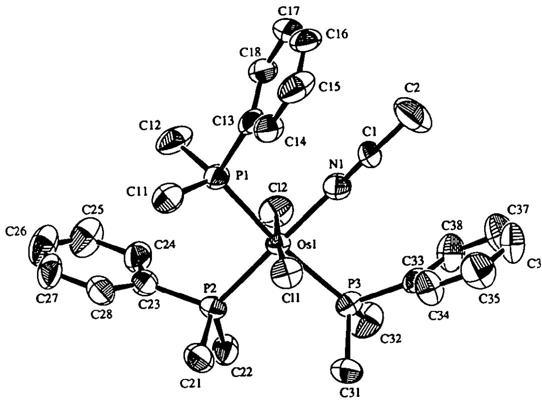


Fig. 1. View of (I) showing the labelling of all non-H atoms. Displacement ellipsoids are shown at the 50% probability level.

Experimental

X-ray quality crystals of (I) were obtained exactly as described by Coombe, Heath, Stephenson, Whitelock & Yellowlees (1985), and their identity as the initial kinetic product confirmed by $^{31}P\{^1H\}$ NMR. For the crystals redissolved in CD_2Cl_2: $P_A = -47.3$ (*t*), $P_B = -35.5$ p.p.m. (*d*) ($^2J_{P-P}$ = 21 Hz).

Crystal data

$[OsCl_2(C_2H_3N)(C_8H_{11}P)_3]$
$M_r = 716.60$
Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å