C(30)	0.3102 (6)	0.1592 (5)	0.3025 (4)	4.4 (2)
C(31)	0.4170 (7)	0.1541 (5)	0.3224 (4)	4.8 (2)
C(32)	0.4639 (7)	0.0837 (6)	0.3415 (4)	4.7 (2)
C(33)	0.4028 (7)	0.0196 (5)	0.3419 (5)	4.8 (3)
C(34)	0.2952 (7)	0.0248 (5)	0.3230 (4)	4.3 (2)
C(35)	−0.0871 (6)	0.1873 (5)	−0.0003 (3)	2.9 (2)
C(36)	−0.1748 (6)	0.2186 (5)	−0.0419 (4)	3.5 (2)
C(37)	−0.2297 (7)	0.1741 (6)	−0.0942 (4)	4.6 (2)
C(38)	−0.1978 (7)	0.1009 (5)	−0.1063 (4)	4.3 (2)
C(39)	−0.1103 (8)	0.0700 (5)	−0.0649 (4)	4.9 (2)
C(40)	−0.0561 (7)	0.1128 (5)	−0.0119 (4)	3.9 (2)
C(41)	−0.0758 (6)	0.3336 (4)	0.0684 (3)	2.8 (2)
C(42)	−0.1354 (7)	0.3454 (5)	0.1150 (4)	3.9 (2)
C(43)	−0.1914 (7)	0.4136 (5)	0.1148 (4)	4.5 (2)
C(44)	−0.1883 (7)	0.4698 (5)	0.0682 (5)	4.6 (2)
C(45)	−0.1312 (7)	0.4593 (5)	0.0219 (4)	3.9 (2)
C(46)	−0.0764 (6)	0.3916 (5)	0.0210 (4)	3.6 (2)
C(47)	0.1021 (6)	0.2725 (5)	0.0325 (4)	3.2 (2)
C(48)	0.1067 (7)	0.2567 (6)	−0.0315 (4)	4.9 (3)
C(49)	0.1887 (9)	0.2840 (7)	−0.0582 (5)	6.3 (3)
C(50)	0.2658 (8)	0.3261 (7)	−0.0205 (6)	6.1 (3)
C(51)	0.2636 (8)	0.3427 (7)	0.0439 (6)	7.2 (3)
C(52)	0.1806 (8)	0.3161 (7)	0.0692 (5)	6.0 (3)

† Partial occupancy (see below).

Table 2. *Selected geometric parameters (Å)*

Re(1)—N(1*ab*)	1.81 (1)	Re(1)—C(1)	2.105 (8)
Re(1)—C(4*b*)	1.64 (3)	Re(1)—C(4*a*)	1.87 (1)
Re(1)—C(7)	2.306 (9)	Re(1)—C(8)	2.309 (9)
Re(1)—C(9)	2.290 (10)	Re(1)—C(10)	2.290 (9)
Re(1)—C(11)	2.328 (9)	Re(2)—P(1)	2.423 (2)
Re(2)—P(2)	2.423 (2)	Re(2)—O(1)	2.180 (5)
Re(2)—O(2)	2.215 (5)	Re(2)—C(5)	1.859 (8)
Re(2)—C(6)	1.868 (8)	P(1)—C(17)	1.829 (8)
P(1)—C(23)	1.832 (8)	P(1)—C(29)	1.847 (8)
P(2)—C(35)	1.834 (7)	P(2)—C(41)	1.831 (8)
P(2)—C(47)	1.835 (8)	O(1)—C(1)	1.302 (8)
O(2)—C(1)	1.285 (8)	O(3*b*)—N(1*ab*)	1.23 (3)
O(3*a*)—N(1*ab*)	1.27 (1)	O(4*b*)—C(4*b*)	1.25 (3)
O(4*a*)—C(4*a*)	1.16 (2)	O(5)—C(5)	1.177 (9)
O(6)—C(6)	1.168 (9)		

Range for phenyl C—C bond distances is 1.35–1.41 Å [average 1.38 (1) Å]. Range for internal Cp* C—C bond distances is 1.40–1.42 Å [average 1.41 (1) Å]. Range for *ipso*-C to Cp* C—C bond distances is 1.47–1.51 Å [average 1.50 (1) Å].

Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV); corrections for anomalous-dispersion effects were made. The structure was solved using heavy-atom Patterson methods (*SAPI91*; Fan, 1991) and expanded using Fourier techniques. All non-H atoms (not involved in the carbonyl or nitrosyl disorder) were refined anisotropically. H atoms were located by Δ maps but were not refined. The carbonyl disorder was modeled with C—O groups of occupancies 2/3 (C4*a*, O4*a*) and 1/3 (C4*b*, O4*b*). The nitrosyl was modeled with a common N atom (N1*ab*) and two O atoms having occupancies of 2/3 (O3*a*) and 1/3 (O3*b*). All computations were performed using the *TEXSAN* package (Molecular Structure Corporation, 1994).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, along with a figure showing the disorder in the molecule, have been deposited with the IUCr (Reference: BK1177). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Two 'Ruthenium-Blue' Precursors: Tri-μ-chloro-hexakis(dimethylphenylarsine)-diruthenium(II) Trifluoromethanesulfonate and Tri-μ-bromo-hexakis(trimethylarsine)-diruthenium(II) Trifluoromethanesulfonate

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Abstract

Confacial bi-octahedral $[Ru_2(\mu\text{-}Cl)_3(AsMe_2Ph)_6]CF_3SO_3$, (1), and $[Ru_2(\mu\text{-}Br)_3(AsMe_3)_6]CF_3SO_3$, (2), are the first tertiary-arsine-capped systems within the wider class of redox-active $[L_3Ru(\mu\text{-}X)_3RuL_3]^{+/2+}$ complexes (L = NR_3, PR_3 or AsR_3; X = Cl or Br) to be structurally characterized. Compounds (1) and (2) have measured internuclear separations and mean bridgehead angles ($Ru^{II}\cdots Ru^{II}$/Ru—X—Ru) of 3.275 (2)/83.5 and 3.413 (1) Å/81.8°, respectively.

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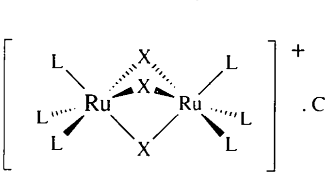
Comment

The crystal structures of the title compounds, (1) and (2), were sought as part of a wider study of mixed valency in redox-active confacial bi-octahedral $[L_3Ru(\mu\text{-}X)_3RuL_3]^{+/2+}$ complexes, where L = NR_3, PR_3 or AsR_3, and X = Cl or Br. These are the first hexakis-arsine-capped examples to be structurally defined and compound (2) also represents the first bromo-bridged X-ray structure, for L = PR_3 as well as AsR_3.



(1) X = Cl; L = $AsMe_2Ph$
(2) X = Br; L = $AsMe_3$

There is no crystallographically imposed symmetry in either binuclear cation, but in both cases coordination in the triply bridged complex approaches regular trigonal (D_{3h}) geometry. The mutual inclinations between the three As–Ru–X–Ru–As planes are all within 2.5° of 120° for compound (1) and within 1° for (2).

Mean values of the most pertinent bond lengths and angles of compound (1) are compared with those of its direct analogue $[Ru_2(\mu\text{-}Cl)_3(PMe_2Ph)_6]^+$ in Table 5. Despite very similar steric relationships in the terminal RuL_3 faces, capping by $AsMe_2Ph$ rather than PMe_2Ph is associated with closure of the bridgehead angle (Ru—Cl—Ru) by 2.5° and overall contraction of the $RuCl_3Ru$ core by approximately 0.1 Å.

The phenyl groups in compound (1) are organized in an interesting fashion; each pair of eclipsed ligands [*i.e.* As(1) and As(4), *etc.*] is oriented so that one phenyl ring lies approximately perpendicular to the other. This edge-to-plane relationship is also achieved between two adjacent ligands [As(3) to As(2)] on Ru(1) and likewise [As(5) to As(6)] on Ru(2).

Surprisingly, $[Ru_2(\mu\text{-}Br)_3(AsMe_3)_6]CF_3SO_3$, (2), represents the first $[Ru_2(\mu\text{-}Br)_3L_6]^+$ cation to be structurally characterized. Being less encumbered than compound (1), it reveals a simplified unit-cell organization, with the Ru—Ru vector accidentally aligned with the c axis.

The increased Ru···Ru separation in compound (2) follows simply from the intrinsic extension in Ru—Br *versus* Ru—Cl bond lengths. For (2), as for (1), a narrower bridgehead angle is found than might be expected from a wide experience of hexakis-phosphine systems such as $[Ru_2(\mu\text{-}Cl)_3(PEt_2Ph)_6]^+$ (Raspin, 1969), $[Ru_2(\mu\text{-}Cl)_3(triphos)_2]^+$ (Rhodes, Sorato, Venanzi & Bachechi, 1988) and $[Ru_2(\mu\text{-}Cl)_3(PBu_3)_6]^+$ (Cotton & Torralba, 1991), where the mean bridgehead angles range from 86 to 88°.

The importance of this structural distinction between the closed-shell AsR_3 and PR_3 complexes is that it appears to carry over to the mixed-valence $[Ru_2(\mu\text{-}Cl)_3(AsR_3)_6]^{2+}$ and $[Ru_2(\mu\text{-}Cl)_3(PR_3)_6]^{2+}$ systems. The one-electron oxidized forms of compounds (1) and (2) have intrinsically stronger metal–metal interactions than their more familiar PR_3 analogues and display classical 'ruthenium-blue' near-IR spectra (Yeomans, Humphrey & Heath, 1995) reminiscent of their structurally characterized ammine counterparts $[Ru_2(\mu\text{-}Cl)_3(NH_3)_6]^{2+}$ (Hughes, O'Reardon, Poole, Hursthouse & Thornton-Pett, 1987) and $[Ru_2(\mu\text{-}Br)_3(NH_3)_6]^{2+}$ (Beattie, Del Favero, Hambley & Hush, 1988). The newly discov-

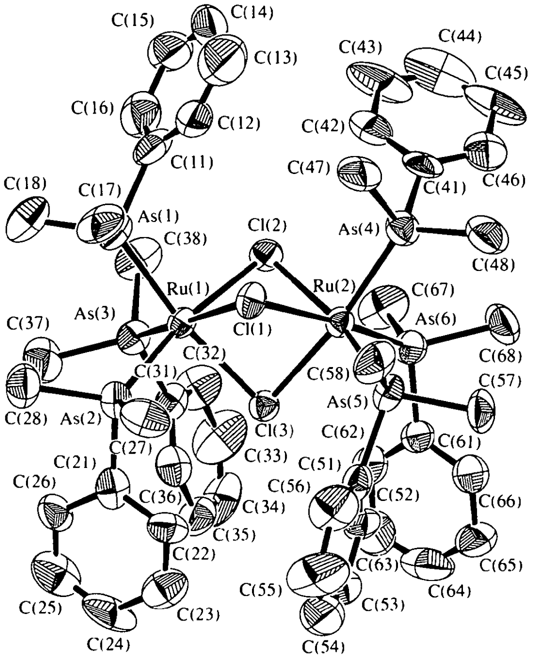


Fig. 1. View of compound (1) showing the labelling of all non-H atoms. Displacement ellipsoids are plotted at the 50% probability level.

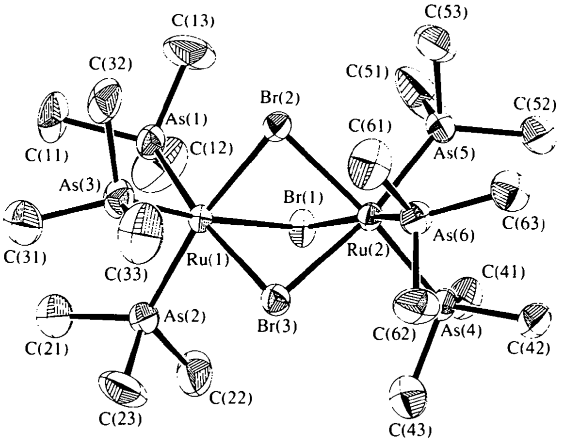


Fig. 2. View of compound (2) showing the labelling of all non-H atoms. Displacement ellipsoids are plotted at the 50% probability level.

ered $[Ru_2(\mu\text{-}X)_3(PMe_3)_6]^{2+}$ (X = Cl, Br) species have near-IR spectra more akin to their arsine analogues than to the generality of $[Ru_2(\mu\text{-}X)_3(PR_3)_6]^{2+}$ complexes. The exceptional bridgehead angle of 82.7° reported for $[Ru_2Cl_3(PMe_3)_6]BF_4$ thus assumes fresh significance. We hope to describe some of the missing $[Ru_2(\mu\text{-}Br)_3(PR_3)_6]CF_3SO_3$ crystal structures shortly (see *Note added in proof*).

Note added in proof. Our latest measurements reveal that $[Ru_2(\mu\text{-}Cl)_3(PMe_3)_6]CF_3SO_3$ is strictly isostructural with its $AsMe_3$ analogue and has Ru· · ·Ru = 3.374 (6), Ru—Cl = 2.50 Å, Ru—Cl—Ru = 85.1 and P—Ru—P = 95.2° (*cf.* Table 5). These seem a more reliable basis for comparison with the title compound than the possibly misleading results for the BF_4^- salt, and point to a consistent contraction of Ru· · ·Ru and X—Ru—X between the corresponding PR_3 and AsR_3 systems.

Experimental

Compounds (1) and (2) were prepared by reaction of $K_3[Ru_2X_9]$ (X = Cl, Br) with the appropriate arsine and subsequent treatment with CF_3SO_3H, as described by Yeomans, Humphrey & Heath (1995). X-ray quality crystals separated from near-saturated 1:3 CH_2Cl_2/Et_2O solutions on cooling.

Compound (1)

Crystal data

$[Ru_2Cl_3(C_8H_{11}As)_6]CF_3SO_3$
M_r = 1550.14
Monoclinic
$P2_1/c$
a = 14.663 (2) Å
b = 16.773 (3) Å
c = 24.441 (3) Å
β = 97.30 (1)°
V = 5962 (1) Å^3
Z = 4
D_x = 1.727 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 25 reflections
θ = 12.9–15.9°
μ = 4.028 mm^{-1}
T = 296 (1) K
Needle
0.29 × 0.09 × 0.09 mm
Orange

Data collection

Rigaku AFC-6S diffractometer
$\omega/2\theta$ scans
Absorption correction: face-indexed analytical correction (de Meulenaer & Tompa, 1965)
$T_{\min}$ = 0.660, $T_{\max}$ = 0.736
8537 measured reflections
8164 independent reflections

4373 observed reflections [$I > 3\sigma(I)$]
$R_{\rm int}$ = 0.035
$\theta_{\max}$ = 22.55°
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 18$
$l = -26 \rightarrow 26$
3 standard reflections monitored every 150 reflections

Refinement

Refinement on F
R = 0.054
wR = 0.055
S = 3.03
4373 reflections
547 parameters
H-atom parameters not refined
$w = 4F_o^2/[\sigma^2(F_o^2) + (0.006F_o^2)^2]$
$(\Delta/\sigma)_{\max}$ = 0.007

$\Delta\rho_{\max}$ = 2.34 e Å^{-3}
$\Delta\rho_{\min}$ = −1.40 e Å^{-3}
Extinction correction: Zachariasen (1967) type II, Gaussian isotropic
Extinction coefficient: 4.1 (6) × 10^{-8}
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 isotropic or equivalent isotropic displacement parameters (Å^2) for (1)*

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

	x	y	z	$U_{\rm eq}/U_{\rm iso}$
Ru(1)	0.8133 (1)	0.61079 (9)	0.76187 (6)	0.0370 (5)
Ru(2)	0.6785 (1)	0.69142 (9)	0.65964 (6)	0.0394 (5)
As(1)	0.8057 (2)	0.6449 (1)	0.85610 (8)	0.0541 (8)
As(2)	0.9764 (1)	0.6273 (1)	0.76901 (9)	0.0482 (7)
As(3)	0.8118 (2)	0.4707 (1)	0.77681 (9)	0.0470 (7)
As(4)	0.5533 (2)	0.7799 (1)	0.67125 (9)	0.0539 (8)
As(5)	0.7435 (2)	0.7769 (1)	0.59683 (8)	0.0515 (8)
As(6)	0.5883 (1)	0.6107 (1)	0.59278 (8)	0.0512 (7)
Cl(1)	0.7836 (3)	0.7520 (3)	0.7361 (2)	0.045 (2)
Cl(2)	0.6457 (3)	0.6068 (3)	0.7377 (2)	0.046 (2)
Cl(3)	0.8048 (3)	0.5975 (3)	0.6620 (2)	0.042 (2)
S(1)	0.7505 (6)	0.1416 (5)	0.4946 (3)	0.239 (6)†
F(1)	0.6463 (10)	0.0277 (8)	0.5167 (6)	0.279 (11)†
F(2)	0.715 (1)	0.0887 (8)	0.5871 (4)	0.193 (8)†
F(3)	0.790 (1)	0.0084 (7)	0.5417 (6)	0.402 (13)†
O(1)	0.760 (1)	0.1121 (8)	0.4416 (3)	0.197 (10)†
O(2)	0.8336 (8)	0.1777 (9)	0.5174 (5)	0.266 (13)†
O(3)	0.6792 (10)	0.1986 (7)	0.4905 (6)	0.304 (13)†
C(1)	0.7235 (7)	0.0613 (5)	0.5379 (4)	0.41 (3)†
C(11)	0.684 (2)	0.664 (2)	0.8747 (9)	0.069 (10)
C(12)	0.644 (2)	0.735 (2)	0.8659 (10)	0.09 (1)
C(13)	0.558 (3)	0.753 (2)	0.877 (1)	0.13 (2)
C(14)	0.509 (3)	0.694 (3)	0.899 (1)	0.13 (2)
C(15)	0.542 (2)	0.623 (2)	0.908 (1)	0.10 (1)
C(16)	0.633 (2)	0.605 (2)	0.894 (1)	0.09 (1)
C(17)	0.863 (2)	0.745 (1)	0.8779 (8)	0.085 (9)
C(18)	0.857 (2)	0.581 (1)	0.9173 (8)	0.081 (9)
C(21)	1.042 (1)	0.562 (1)	0.7216 (9)	0.055 (8)
C(22)	1.032 (1)	0.576 (1)	0.6648 (10)	0.059 (8)
C(23)	1.075 (2)	0.525 (2)	0.6319 (9)	0.08 (1)
C(24)	1.129 (2)	0.463 (2)	0.653 (1)	0.09 (1)
C(25)	1.140 (2)	0.449 (2)	0.708 (1)	0.09 (1)
C(26)	1.100 (2)	0.499 (1)	0.7434 (9)	0.068 (9)
C(27)	1.014 (1)	0.729 (1)	0.7476 (9)	0.077 (9)
C(28)	1.057 (1)	0.614 (1)	0.8388 (8)	0.076 (9)
C(31)	0.805 (2)	0.401 (1)	0.7127 (8)	0.050 (7)
C(32)	0.734 (2)	0.348 (2)	0.6981 (10)	0.08 (1)
C(33)	0.737 (2)	0.297 (2)	0.654 (1)	0.11 (1)
C(34)	0.805 (2)	0.300 (2)	0.622 (1)	0.09 (1)
C(35)	0.877 (2)	0.356 (1)	0.6336 (9)	0.077 (10)
C(36)	0.873 (1)	0.404 (1)	0.6790 (9)	0.057 (8)
C(37)	0.910 (2)	0.418 (1)	0.8232 (9)	0.082 (9)
C(38)	0.705 (2)	0.437 (1)	0.8104 (8)	0.077 (9)
C(41)	0.439 (2)	0.732 (1)	0.686 (1)	0.067 (9)
C(42)	0.435 (2)	0.689 (2)	0.736 (1)	0.08 (1)
C(43)	0.358 (2)	0.649 (2)	0.750 (2)	0.13 (2)
C(44)	0.282 (2)	0.650 (2)	0.714 (2)	0.13 (2)
C(45)	0.278 (2)	0.696 (2)	0.664 (1)	0.10 (1)
C(46)	0.357 (2)	0.734 (1)	0.6501 (9)	0.075 (9)
C(47)	0.578 (1)	0.851 (1)	0.7339 (8)	0.079 (9)
C(48)	0.508 (1)	0.861 (1)	0.6164 (9)	0.087 (10)
C(51)	0.858 (1)	0.745 (1)	0.5706 (8)	0.049 (8)
C(52)	0.862 (1)	0.674 (2)	0.5407 (8)	0.064 (9)
C(53)	0.939 (2)	0.650 (2)	0.5193 (9)	0.077 (10)
C(54)	1.014 (2)	0.696 (2)	0.523 (1)	0.12 (1)
C(55)	1.012 (2)	0.769 (2)	0.552 (1)	0.13 (2)
C(56)	0.935 (2)	0.791 (2)	0.5772 (10)	0.09 (1)
C(57)	0.676 (1)	0.805 (1)	0.5264 (8)	0.071 (8)
C(58)	0.778 (2)	0.879 (1)	0.6299 (8)	0.078 (9)
C(61)	0.649 (1)	0.557 (1)	0.5380 (8)	0.049 (8)
C(62)	0.697 (2)	0.486 (2)	0.5507 (9)	0.070 (9)
C(63)	0.742 (2)	0.443 (2)	0.510 (1)	0.10 (1)

C(64)	0.734 (2)	0.475 (2)	0.460 (1)	0.10 (1)
C(65)	0.689 (2)	0.544 (2)	0.4449 (10)	0.09 (1)
C(66)	0.644 (1)	0.583 (1)	0.4848 (10)	0.064 (8)
C(67)	0.530 (1)	0.522 (1)	0.6241 (9)	0.090 (10)
C(68)	0.482 (1)	0.650 (1)	0.5442 (8)	0.085 (9)

† U_{iso}.

Table 2. *Selected geometric parameters (Å, °) for (1)*

Ru(1)—As(1)	2.389 (3)	Ru(2)—As(4)	2.405 (3)
Ru(1)—As(2)	2.391 (2)	Ru(2)—As(5)	2.386 (3)
Ru(1)—As(3)	2.378 (3)	Ru(2)—As(6)	2.388 (3)
Ru(1)—Cl(1)	2.476 (5)	Ru(2)—Cl(1)	2.484 (5)
Ru(1)—Cl(2)	2.455 (4)	Ru(2)—Cl(2)	2.474 (5)
Ru(1)—Cl(3)	2.439 (5)	Ru(2)—Cl(3)	2.427 (5)
As(1)—Ru(1)—As(2)	94.06 (8)	As(5)—Ru(2)—As(6)	97.61 (9)
As(1)—Ru(1)—As(3)	94.93 (9)	Cl(1)—Ru(2)—Cl(2)	79.5 (2)
As(2)—Ru(1)—As(3)	97.59 (8)	Cl(1)—Ru(2)—Cl(3)	81.3 (2)
Cl(1)—Ru(1)—Cl(2)	80.0 (2)	Cl(2)—Ru(2)—Cl(3)	80.3 (2)
Cl(1)—Ru(1)—Cl(3)	81.3 (2)	Ru(1)—Cl(1)—Ru(2)	82.7 (1)
Cl(2)—Ru(1)—Cl(3)	80.5 (2)	Ru(1)—Cl(2)—Ru(2)	83.3 (2)
As(4)—Ru(2)—As(5)	94.51 (10)	Ru(1)—Cl(3)—Ru(2)	84.6 (2)
As(4)—Ru(2)—As(6)	93.79 (9)		

Compound (2)

Crystal data

$[Ru_2Br_3(C_3H_9As)_6]CF_3SO_3$
M_r = 1311.07
Monoclinic
$P2_1/c$
a = 10.670 (4) Å
b = 14.742 (4) Å
c = 26.253 (3) Å
β = 91.14 (2)°
V = 4128 (1) Å^3
Z = 4
D_x = 2.109 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 25 reflections
θ = 11.1–12.8°
μ = 8.501 mm^{-1}
T = 296 (1) K
Block
0.16 × 0.08 × 0.08 mm
Orange

Data collection

Rigaku AFC-6*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical using azimuthal ψ-scan data (North, Phillips & Mathews, 1968)
$T_{\min}$ = 0.85, $T_{\max}$ = 1.00
6176 measured reflections
5749 independent reflections

2876 observed reflections [$I > 3\sigma(I)$]
R_{int} = 0.049
$\theta_{\max}$ = 24.99°
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 17$
$l = -31 \rightarrow 31$
3 standard reflections monitored every 150 reflections

Refinement

Refinement on F
R = 0.034
wR = 0.025
S = 1.46
2876 reflections
335 parameters
H-atom parameters not refined
$w = 4F_o^2/[\sigma^2(F_o^2) + (0.002F_o^2)^2]$
$(\Delta/\sigma)_{\max}$ = 0.001

$\Delta\rho_{\max}$ = 0.37 e Å^{-3}
$\Delta\rho_{\min}$ = −0.26 e Å^{-3}
Extinction correction: Zachariasen (1967) type II, Gaussian isotropic
Extinction coefficient: 7 (1) × 10^{-9}
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (2)*

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

	x	y	z	U_{eq}
Ru(1)	0.68938 (9)	0.68550 (8)	0.36326 (4)	0.0314 (3)
Ru(2)	0.69850 (10)	0.68318 (8)	0.23338 (4)	0.0308 (3)
Br(1)	0.8760 (1)	0.7041 (1)	0.30229 (5)	0.0419 (5)
Br(2)	0.6235 (1)	0.56035 (10)	0.29735 (5)	0.0428 (5)
Br(3)	0.5795 (1)	0.78909 (10)	0.29548 (5)	0.0409 (5)
As(1)	0.8204 (1)	0.5877 (1)	0.41310 (6)	0.0471 (5)
As(2)	0.7359 (1)	0.8181 (1)	0.41170 (5)	0.0456 (5)
As(3)	0.5052 (1)	0.6526 (1)	0.40855 (6)	0.0524 (6)
As(4)	0.7930 (1)	0.8025 (1)	0.18715 (5)	0.0424 (5)
As(5)	0.8044 (1)	0.5667 (1)	0.18851 (6)	0.0433 (5)
As(6)	0.5138 (1)	0.6789 (1)	0.18076 (5)	0.0424 (5)
S(1)	0.8431 (5)	0.2805 (4)	0.9442 (2)	0.085 (2)
F(1)	0.906 (1)	0.4281 (8)	0.9908 (5)	0.136 (6)
F(2)	0.844 (1)	0.3274 (9)	1.0383 (4)	0.146 (6)
F(3)	0.718 (1)	0.4016 (8)	0.9948 (4)	0.125 (5)
O(1)	0.747 (1)	0.2205 (9)	0.9515 (6)	0.148 (7)
O(2)	0.824 (1)	0.336 (1)	0.8987 (5)	0.148 (7)
O(3)	0.965 (1)	0.2486 (9)	0.9497 (4)	0.093 (5)
C(1)	0.825 (2)	0.360 (1)	0.9918 (8)	0.083 (8)
C(11)	0.788 (1)	0.553 (1)	0.4844 (5)	0.080 (7)
C(12)	0.993 (1)	0.623 (1)	0.4226 (7)	0.105 (8)
C(13)	0.845 (2)	0.469 (1)	0.3850 (7)	0.095 (8)
C(21)	0.780 (1)	0.817 (1)	0.4842 (5)	0.073 (6)
C(22)	0.866 (2)	0.896 (1)	0.3853 (6)	0.091 (7)
C(23)	0.599 (2)	0.908 (1)	0.4155 (6)	0.095 (7)
C(31)	0.486 (1)	0.684 (1)	0.4798 (6)	0.082 (6)
C(32)	0.464 (1)	0.521 (1)	0.4145 (6)	0.075 (6)
C(33)	0.350 (1)	0.693 (1)	0.3774 (6)	0.098 (7)
C(41)	0.974 (1)	0.800 (1)	0.1876 (5)	0.066 (6)
C(42)	0.762 (1)	0.822 (1)	0.1143 (5)	0.061 (5)
C(43)	0.763 (1)	0.925 (1)	0.2115 (5)	0.068 (6)
C(51)	0.961 (2)	0.529 (1)	0.2187 (6)	0.113 (8)
C(52)	0.854 (1)	0.580 (1)	0.1190 (6)	0.066 (6)
C(53)	0.722 (2)	0.453 (1)	0.1842 (6)	0.086 (7)
C(61)	0.381 (1)	0.603 (1)	0.2035 (6)	0.078 (7)
C(62)	0.425 (1)	0.7924 (10)	0.1731 (5)	0.072 (6)
C(63)	0.519 (1)	0.6435 (10)	0.1094 (5)	0.059 (6)

Table 4. *Selected geometric parameters (Å, °) for (2)*

Ru(1)—Br(1)	2.594 (2)	Ru(2)—Br(1)	2.611 (2)
Ru(1)—Br(2)	2.616 (2)	Ru(2)—Br(2)	2.606 (2)
Ru(1)—Br(3)	2.606 (2)	Ru(2)—Br(3)	2.606 (2)
Ru(1)—As(1)	2.382 (2)	Ru(2)—As(4)	2.373 (2)
Ru(1)—As(2)	2.380 (2)	Ru(2)—As(5)	2.380 (2)
Ru(1)—As(3)	2.367 (2)	Ru(2)—As(6)	2.385 (2)
Br(1)—Ru(1)—Br(2)	82.27 (5)	Br(2)—Ru(2)—Br(3)	81.58 (5)
Br(1)—Ru(1)—Br(3)	81.79 (5)	As(4)—Ru(2)—As(5)	94.06 (6)
Br(2)—Ru(1)—Br(3)	81.39 (5)	As(4)—Ru(2)—As(6)	94.47 (7)
As(1)—Ru(1)—As(2)	95.18 (7)	As(5)—Ru(2)—As(6)	95.11 (7)
As(1)—Ru(1)—As(3)	94.80 (7)	Ru(1)—Br(1)—Ru(2)	81.96 (5)
As(2)—Ru(1)—As(3)	93.82 (6)	Ru(1)—Br(2)—Ru(2)	81.63 (5)
Br(1)—Ru(2)—Br(2)	82.13 (5)	Ru(1)—Br(3)—Ru(2)	81.82 (5)
Br(1)—Ru(2)—Br(3)	81.47 (6)		

Table 5. *Comparison of the mean dimensions (Å, °) of four related $[Ru_2(\mu\text{-}X)_3L_6]^+$ complexes*

	Ru···Ru	Ru—X	Ru—X—Ru	Ru—L	L—Ru—L
$[Ru_2Br_3(AsMe_3)_6]^{+\,a}$	3.413 (1)	2.61	81.8	2.38	94.6
$[Ru_2Cl_3(AsMe_2Ph)_6]^{+\,a}$	3.275 (2)	2.46	83.5	2.39	95.4
$[Ru_2Cl_3(PMe_2Ph)_6]^{+\,b}$	3.39	2.49	86	2.29	95
$[Ru_2Cl_3(PMe_3)_6]^{+\,c,d}$	3.275	2.48	82.7	2.25	95.4

References: (*a*) this work; (*b*) Laing & Pope (1976); (*c*) Statler, Wilkinson, Thornton-Pett & Hursthouse (1984); (*d*) but see *Note added in proof*.

The θ-scan widths used were $(1.00 + 0.3\tan\theta)^\circ$ for (1) and $(0.90 + 0.3\tan\theta)^\circ$ for (2), both at a speed of 4.0° $\min^{-1}$ (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 difference maps and fixed in ideal positions with $U_{iso} = 1.2U_{eq}(C)$. All non-H atoms were refined anisotropically in both cases, with the exception that in (1) the ill-behaved trifluoromethanesulfonate counterion was refined as a rigid group with individual isotropic displacement parameter values. The largest peaks in the final difference map for compound (1) lie very close to the heaviest atoms. The structures were solved by Patterson methods and expanded using Fourier techniques (*PATTY* in *DIRDIF*; Beurskens *et al.*, 1992). All calculations were performed using *TEXSAN* (Molecular Structure Corporation, 1993). *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1989) was used for data collection and cell refinement.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: TA1055). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tris(4,4'-bipyrimidine)ruthenium(II) Bis(hexafluorophosphate) Acetone Solvate

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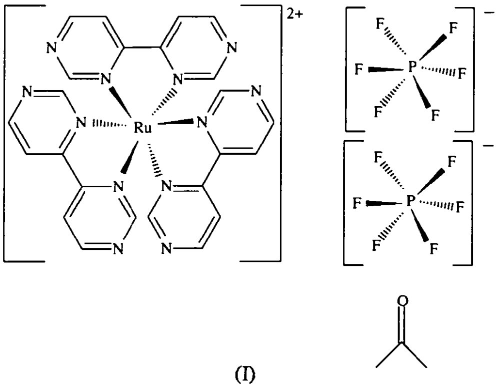
Abstract

The molecular structure of tris(4,4'-bipyrimidine)-ruthenium(II) $\{[Ru(bpm)_3]^{2+}\}$ in the title compound $\{[Ru(C_8H_6N_4)_3](PF_6)_2.C_3H_6O\}$ is similar to that of tris(2,2'-bipyridine)ruthenium(II) $\{[Ru(bpy)_3]^{2+}\}$. However, replacement of C by N in the heterocyclic ring alters the molecular electrostatic potential of the complex cation and hence the chiral recognition and self-assembling, yielding a crystal-packing pattern that is unique among known structures of related trisdiimine–metal complexes.

Comment

In the course of our work on chiral recognition among trisdiimine–metal complexes (Breu & Catlow, 1995), the crystal structure of the title compound, (I), was determined in order to explore the influence of the molecular electrostatic potential (MEP) on chiral recognition and self-assembling in the crystalline state. Moreover, the lowest electronically excited states of these metal complexes have been studied intensively (*e.g.* Yersin, Huber & Wiedenhofer, 1994).



(I)

A comparison of the crystal structures of the hexafluorophosphate salts of $[Ru(bpy)_3]^{2+}$, $[Ru(bpym)_3]^{2+}$ and $[Ru(bpz)_3]^{2+}$ (bpym = 2,2'-bipyrimidine, bpz = 2,2'-