

X-ray analysis were obtained by slow diffusion of hexanes into a CH₂Cl₂ solution of (I).

Crystal data

[ReBr(C ₅ H ₅)(C ₆ HF ₄)(CO) ₂]	Mo K α radiation
$M_r = 536.29$	$\lambda = 0.71073 \text{ \AA}$
Monoclinic	Cell parameters from 25 reflections
$P2_1/n$	$\theta = 7.5\text{--}12.5^\circ$
$a = 7.864 (2) \text{ \AA}$	$\mu = 12.262 \text{ mm}^{-1}$
$b = 6.964 (2) \text{ \AA}$	$T = 293 (2) \text{ K}$
$c = 24.361 (6) \text{ \AA}$	Needle
$\beta = 97.74 (2)^\circ$	$0.48 \times 0.16 \times 0.12 \text{ mm}$
$V = 1321.9 (5) \text{ \AA}^3$	Intense orange
$Z = 4$	
$D_x = 2.695 \text{ Mg m}^{-3}$	
D_m not measured	

Data collection

Siemens R3 diffractometer	1802 reflections with $I > 2\sigma(I)$
$\theta/2\theta$ scans	$R_{\text{int}} = 0.016$
Absorption correction:	$\theta_{\text{max}} = 25^\circ$
ψ scan (XPREP in SHELXTL/PC; Sheldrick, 1991)	$h = 0 \rightarrow 9$
$T_{\text{min}} = 0.04, T_{\text{max}} = 0.23$	$k = 0 \rightarrow 8$
2385 measured reflections	$l = -28 \rightarrow 20$
2234 independent reflections	2 standard reflections every 98 reflections
	intensity decay: <1%

Refinement

Refinement on F^2	$\Delta\rho_{\text{max}} = 1.31 \text{ e \AA}^{-3}$
$R[F^2 > 2\sigma(F^2)] = 0.034$	$\Delta\rho_{\text{min}} = -1.23 \text{ e \AA}^{-3}$
$wR(F^2) = 0.088$	Extinction correction:
$S = 1.011$	SHELXL97 (Sheldrick, 1997)
2234 reflections	Extinction coefficient:
191 parameters	0.0029 (3)
H-atom parameters constrained	Scattering factors from International Tables for Crystallography (Vol. C)
$w = 1/[\sigma^2(F_o^2) + (0.06P)^2]$	
where $P = (F_o^2 + 2F_c^2)/3$	
$(\Delta/\sigma)_{\text{max}} < 0.01$	

Table 1. Selected bond lengths (\AA)

Re1—C1	1.949 (9)	Re1—C11	2.297 (9)
Re1—C2	1.960 (9)	Re1—C10	2.310 (9)
Re1—C3	2.172 (8)	Re1—C9	2.318 (8)
Re1—C12	2.229 (9)	Re1—Br1	2.6113 (11)
Re1—C13	2.241 (9)		

The title structure was difficult to solve with the uncorrected raw data, and only when a careful absorption correction was performed was it possible to solve it through direct methods and refine it properly by least squares on F^2 . A measure of the importance of the correction can be seen in some final parameters calculated with corrected and uncorrected data, viz the R indexes (0.034 and 0.107), the residual electron density around the Re atom (+1.31/−1.23 and +8.45/−9.52 e \AA^{-3}) etc. Non-H atoms were refined anisotropically, whereas H atoms were idealized (C—H 0.93 \AA) and allowed to ride with isotropic displacement factors 1.2 times larger than those of their hosts. The final residual electron density, though rather large in relative terms, is not unusual in structural studies of organometallic rhenium complexes.

Data collection: P3/P4-PC Diffractometer Program (Siemens, 1991). Cell refinement: P3/P4-PC Diffractometer Program. Data reduction: XDISK in SHELXTL/PC (Sheldrick, 1991). Program(s) used to solve structure: SHELXS97 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL97 (Sheldrick, 1997). Molecular graphics: XP in SHELXTL/PC. Software used to prepare material for publication: PARST (Nardelli, 1983).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1143). Services for accessing these data are described at the back of the journal.

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A cylindrical macrocycle with two caesium cations sandwiched between two diaza-18-crown-6 macrocycles

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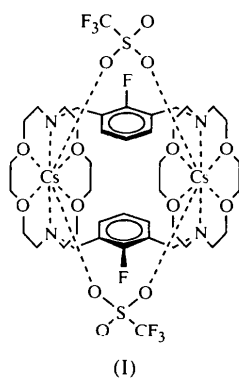
Abstract

Colorless crystals of [51,52-difluoro-12,15,29,32,37,40,45,48-octaoxa-1,9,18,26-tetraazapentacyclo[26.8.8.^{9,18}.-1^{3,7}.1^{20,24}]dopentaconta-3,5,7(51),20,22,24(52)-hexaene-1 κ^6 N¹,N²⁶,O²⁹,O³²,O³⁷,O⁴⁰;2 κ^6 N⁹,N¹⁸,O¹²,O¹⁵,O⁴⁵,O⁴⁸]-

dicaesium bis(trifluoromethanesulfonate), $[\text{Cs}_2(\text{C}_2\text{F}_6\text{O}_6\text{S}_2)_2(\text{C}_{40}\text{H}_{62}\text{F}_2\text{N}_4\text{O}_8)]$, are formed upon slowly allowing diethyl ether to diffuse into an acetonitrile solution of the complex. In the crystal, each caesium cation is coordinated by four O and two N atoms of the crown ether in an irregular fashion. The two metal ions are connected by two bridging bidentate trifluoromethanesulfonate anions leading to a coordination number of eight for each metal ion.

Comment

We have demonstrated in a number of publications that CF units in fluorocarbons can act as efficient donor atoms towards group I and II metal cations (Plenio, 1997). In the course of our work, a number of fluoro cryptands were prepared in order to investigate in some detail the coordinating properties of CF units. Upon synthesizing fluoro cryptands, which typically are (1+1)-addition products of a diaza-crown ether and 2-fluoro-1,3-xylylene dibromide, smaller amounts of the (2+2)-addition product are inevitably formed. These cylindrical macrocycles can also form stable metal complexes and we were interested in whether CF-metal contacts are observed in such compounds.



Consequently, we crystallized the complex, (I), of the cylindrical macrocycle bis[(*N,N'*-diazia-18-crown-6)(2-fluoro-1,3-xylyl)] with two equivalents of caesium trifluoromethanesulfonate by allowing diethyl ether to diffuse into a solution of the complex in acetonitrile over several days. In the crystal, the complex exists as a barrel-shaped molecule with approximate outer dimensions of $0.126 \times 0.096 \text{ \AA}$. Both caesium ions are coordinated within the cavity of the ligand, even though the individual caesium ions are much too large to be located within the center of the diaza-18-crown-6 rings. The coordination sphere of the two caesium ions is completed by the two CF_3SO_3 counter-ions, which form two μ_2 -bridges *via* oxygen to link the metal centers, with a $\text{Cs} \cdots \text{Cs}$ distance of $5.689(6) \text{ \AA}$. The two metal ions are symmetry related *via* an inversion center. Each caesium is in an irregular environment of

six coordinating O atoms: $\text{Cs}-\text{O}1$ $3.234(3)$, $\text{Cs}-\text{O}2$ $3.125(3)$, $\text{Cs}-\text{O}3$ $3.247(3)$ and $\text{Cs}-\text{O}4$ $3.155(3) \text{ \AA}$. Two weaker contacts to nitrogen [$\text{Cs}-\text{N}1$ $3.484(4)$ and $\text{Cs}-\text{N}2$ $3.401(4) \text{ \AA}$] also contribute to the coordination sphere of the metal ion, even though two short distances to C atoms [$\text{Cs}-\text{C}5$ $3.498(4)$ and $\text{Cs}-\text{C}3a$ $3.573(4) \text{ \AA}$; symmetry code: $(a) \frac{1}{2} - x, \frac{3}{2} - y, 1 - z$] are only slightly longer.

Obviously there are no close contacts between the caesium cation and CF units, which is quite surprising as the ^{19}F NMR signal of the ligand shifts from $\delta = -124.50$ to -120.55 p.p.m. upon formation of the metal complex. While it is well known that ^{19}F NMR shifts also depend on conformational properties, it was unexpected that the X-ray crystal structure of the ligand (Plenio & Diodone, 1996a) and of the caesium complex would be similar. An explanation for this could be that the position of the F atom with respect to the aromatic ring current is critical for its ^{19}F NMR shift.

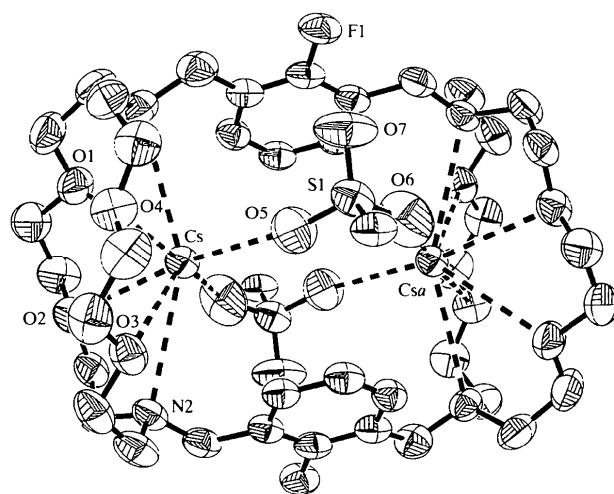


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity and atom Csa is at $\frac{1}{2} - x, \frac{3}{2} - y, 1 - z$.

Experimental

The cylindrical macrocycle was prepared according to Plenio & Diodone (1996b). The corresponding caesium complex was prepared by dissolving a mixture of two equivalents of dry caesium trifluoromethanesulfonate and one equivalent of ligand in acetonitrile. Slow diffusion of diethyl ether onto this solution produced colorless cube-like crystals after several days.

Crystal data

$[\text{Cs}_2(\text{C}_2\text{F}_6\text{O}_6\text{S}_2)_2\text{-(C}_{40}\text{H}_{62}\text{F}_2\text{N}_4\text{O}_8)]$
 $M_r = 1328.90$
 Monoclinic
 $C2/c$

Mo $K\alpha$ radiation
 $\lambda = 0.71069 \text{ \AA}$
 Cell parameters from 25 reflections
 $\theta = 2.3\text{--}18.3^\circ$

$a = 21.331(4) \text{ \AA}$
 $b = 12.203(2) \text{ \AA}$
 $c = 20.881(4) \text{ \AA}$
 $\beta = 92.26(3)^\circ$
 $V = 5431.1(17) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.625 \text{ Mg m}^{-3}$
 D_m not measured

$\mu = 1.509 \text{ mm}^{-1}$
 $T = 293(2) \text{ K}$
 Cube
 $0.4 \times 0.4 \times 0.3 \text{ mm}$
 Colorless

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Data collection

Enraf–Nonius CAD-4
 diffractometer
 ω - 2θ scans
 Absorption correction:
 empirical ψ scan (North
et al., 1968)
 $T_{\min} = 0.485$, $T_{\max} = 0.636$
 5459 measured reflections
 5312 independent reflections

4121 reflections with
 $I > 2\sigma(I)$
 $R_{\text{int}} = 0.043$
 $\theta_{\max} = 25.99^\circ$
 $h = 0 \rightarrow 26$
 $k = -15 \rightarrow 0$
 $l = -25 \rightarrow 25$
 2 standard reflections
 frequency: 60 min
 intensity decay: 2.5%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.107$
 $S = 1.046$
 5312 reflections
 325 parameters
 H atoms treated by a
 mixture of independent
 and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0582P)^2 + 9.4283P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.982 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.596 \text{ e \AA}^{-3}$
 Extinction correction: none
 Scattering factors from
International Tables for Crystallography (Vol. C)

Refinement of the crystal structure in the non-centrosymmetric space group *Cc* did not lead to reasonable results, and in accordance with the *C2* (twofold axis) molecular symmetry, the centrosymmetric setting *C2/c* was therefore considered correct. Data reduction and decay correction used *CADFOR/CADSEX* (Keller, 1993).

Data collection: *TURBOMOLE* in *CAD-4 EXPRESS* (Enraf–Nonius, 1993). Cell refinement: *TURBOMOLE* in *CAD-4 EXPRESS*. Data reduction: *CADFOR/CADSEX*. Program(s) used to solve structure: *SHELX97* (Sheldrick, 1997). Program(s) used to refine structure: *SHELX97*. Molecular graphics: *SCHAKAL* (Keller, 1995). Software used to prepare material for publication: *CIFTAB* in *SHELX97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1299). Services for accessing these data are described at the back of the journal.

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Bis(terpyridine)ruthenium(II) bis(hexafluorophosphate) diacetonitrile solvate

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Abstract

The crystal structure of the title compound, bis(2,2':6',2''-terpyridine)ruthenium(II) bis(hexafluorophosphate) diacetonitrile solvate, with the composition [Ru(C₁₅H₁₁N₃)₂](PF₆)₂·2C₂H₃N is described. The pseudo-octahedral Ru complex has a *C_{2v}* point symmetry, imposed by the geometry constraints of the two identical tridentate ligands. The tetragonal unit cell, with its remarkably long *c* axis [49.306(3) Å], contains two symmetry-independent formula units.

Comment

The coordination compounds formed by ruthenium(II) with polypyridine ligands such as 2,2'-bipyridine (bpy) or 2,2':6',2''-terpyridine (terpy) are among the most commonly used photoactive substances in artificial photosynthesis and photoinduced electron-transfer studies (Kalayanasundaram, 1992; Roundhill, 1994). Recent attempts to utilize Ru complexes of this type as photosensitizers in different applications, such as Grätzel-type solar-cell devices, have been successful in many aspects (Zakeeruddin *et al.*, 1997). Ru–polypyridine complexes can also act as photoactive synthons in nanometer-sized

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