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

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

	x	y	z	$U_{\rm eq}$
Cu	0.18516 (3)	0.05095 (1)	0.12858 (2)	0.02618 (7)
N1	0.0833 (3)	0.00157 (11)	0.27710 (15)	0.0338 (3)
N2	0.2328 (2)	0.17316 (10)	0.23040 (13)	0.0284 (3)
N3	0.3585 (2)	0.11378 (11)	0.0247 (2)	0.0346 (3)
C1	0.0746 (4)	0.0806 (2)	0.3661 (2)	0.0455 (4)
C2	0.2501 (4)	0.14821 (14)	0.3648 (2)	0.0412 (4)
C3	0.4157 (3)	0.21983 (13)	0.2053 (2)	0.0372 (4)
C4	0.3925 (3)	0.21528 (13)	0.0636 (2)	0.0419 (4)
Cl	0.17170 (6)	−0.09649 (3)	0.02918 (4)	0.03071 (9)
N4	0.5780 (2)	−0.10128 (12)	0.29428 (14)	0.0380 (3)
O1	0.4514 (2)	−0.12719 (12)	0.35345 (15)	0.0499 (4)
O2	0.5907 (3)	−0.01556 (14)	0.2662 (2)	0.0689 (5)
O3	0.6891 (4)	−0.1599 (2)	0.2604 (2)	0.0907 (8)

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

Cu—N3	2.004 (2)	N2—C2	1.472 (2)
Cu—N1	2.014 (2)	N3—C4	1.483 (2)
Cu—N2	2.017 (1)	C1—C2	1.509 (3)
Cu—Cl	2.318 (1)	C3—C4	1.503 (3)
Cu—Cl$^{\rm i}$	2.646 (1)	Cl—Cu$^{\rm i}$	2.646 (1)
Cu—Cu$^{\rm i}$	3.537 (1)	N4—O3	1.221 (2)
N1—C1	1.476 (2)	N4—O1	1.233 (2)
N2—C3	1.468 (2)	N4—O2	1.246 (3)
N3—Cu—N1	162.27 (7)	C3—N2—Cu	107.66 (10)
N3—Cu—N2	84.18 (6)	C2—N2—Cu	107.57 (11)
N1—Cu—N2	83.94 (6)	C4—N3—Cu	109.30 (11)
N3—Cu—Cl	95.31 (5)	N1—C1—C2	108.0 (2)
N1—Cu—Cl	94.71 (4)	N2—C2—C1	106.6 (2)
N2—Cu—Cl	172.32 (4)	N2—C3—C4	106.73 (15)
N3—Cu—Cl$^{\rm i}$	94.93 (5)	N3—C4—C3	107.46 (15)
N1—Cu—Cl$^{\rm i}$	99.77 (5)	Cu—Cl—Cu$^{\rm i}$	90.62 (1)
N2—Cu—Cl$^{\rm i}$	98.30 (4)	O3—N4—O1	120.2 (2)
Cl—Cu—Cl$^{\rm i}$	89.38 (2)	O3—N4—O2	119.4 (2)
C1—N1—Cu	109.8 (1)	O1—N4—O2	120.4 (2)
C3—N2—C2	114.9 (2)		

Symmetry code: (i) $-x, -y, -z$.

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
N1—HN1···O1	0.87 (2)	2.17 (3)	2.996 (7)	159 (3)
N2—HN2···O1$^{\rm i}$	0.89 (2)	2.39 (2)	3.098 (2)	137 (2)
N1—HN11···O3$^{\rm ii}$	0.90 (3)	2.60 (3)	3.441 (3)	157 (2)
N1—HN11···O2$^{\rm ii}$	0.90 (3)	2.48 (3)	3.272 (3)	146 (2)
N3—HN31···O3$^{\rm iii}$	0.88 (2)	2.29 (3)	3.089 (3)	151 (2)
N3—HN3···Cl$^{\rm iii}$	0.88 (2)	2.63 (3)	3.338 (2)	138 (2)

Symmetry codes: (i) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (ii) $x-1, y, z$; (iii) $1-x, -y, -z$.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *Xtal*3.2 (Hall, Flack & Stewart, 1992). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *PARST* (Nardelli, 1983).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1250). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Paucity of Hydrogen Bonds in Ferrocene-1,1′-diylbis[bis(4-methoxyphenyl)methanol]–Methanol (3/2)

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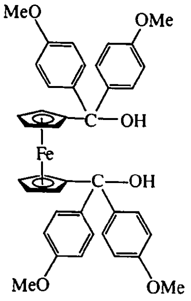
Abstract

In the 3:2 adduct formed between ferrocene-1,1′-diylbis[bis(4-methoxyphenyl)methanol] and methanol, $3[\mathrm{Fe(C_{20}H_{19}O_3)_2}].2\mathrm{CH_4O}$, the ferrocenediol occupies two types of site. Ferrocenediol molecules in general positions form intramolecular O—H···O hydrogen bonds and are hydrogen-bonded to methanol molecules by a single O—H···O hydrogen bond, while ferrocenediol molecules lying across centres of inversion form no O—H···O hydrogen bonds. Overall, only half of the hydroxyl groups in the asymmetric unit act as donors in O—H···O hydrogen bonds, while none of the seven independent methoxy groups acts as acceptors of O—H···O hydrogen bonds.

Comment

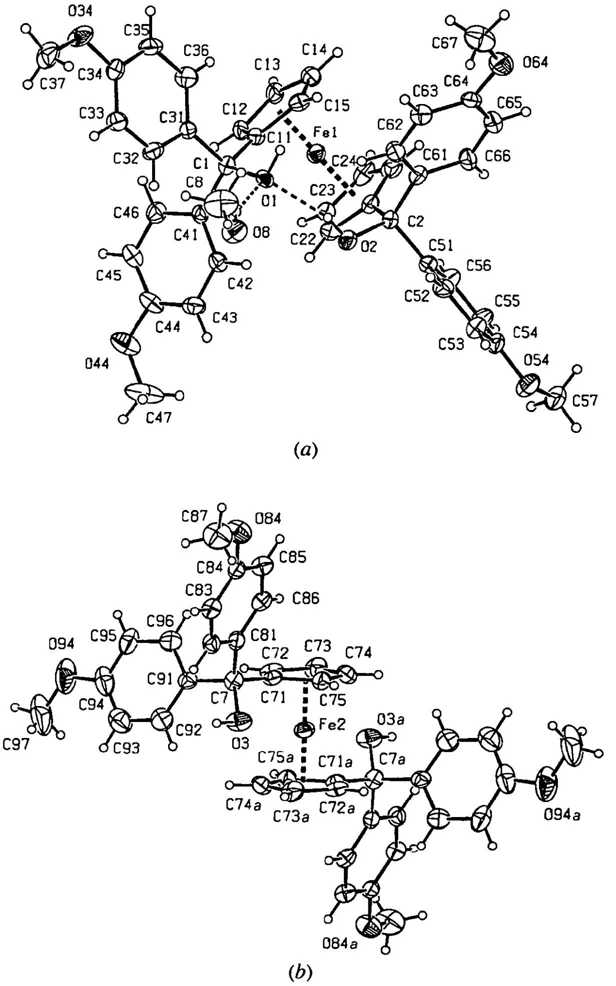
Ferrocene-1,1′-diylbis[bis(4-methoxyphenyl)methanol], $[Fe\{C_5H_4C(OH)(C_6H_4OCH_3)_2\}_2]$, (I), is closely related to ferrocene-1,1′-diylbis(diphenylmethanol), $[Fe\{C_5H_4\text{-}C(OH)Ph_2\}_2]$, (II) (Ferguson, Gallagher, Glidewell & Zakaria, 1993*a*; Aliev *et al.*, 1995), differing in that it contains an additional four sites per molecule which are potential hydrogen-bond acceptors.



(I)

The impetus towards the structural study of (I) is twofold. Firstly, the simpler analogue, (II), exhibits a rich variety of host–guest behaviour (Ferguson, Gallagher, Glidewell & Zakaria, 1993*b*; Glidewell, Ferguson, Lough & Zakaria, 1994) in which the host–guest interactions are all hydrogen bonds of the O—H···O, O—H···N and C—H···π(arene) types, and secondly, the incorporation of 4-methoxy substituents effects major structural changes in triarylmethanols. Triphenylmethanol, Ph_3COH, (III), thus crystallizes as tetrahedral tetramers (Ferguson, Gallagher, Glidewell, Low & Scrimgeour, 1992), whereas tris(4-methoxyphenyl)methanol, $(CH_3OC_6H_4)_3COH$, (IV), crystallizes as open dimers in which the hydrogen bonding involves only one of the two methoxy groups and only one of the two hydroxyl groups in each dimer (Ferguson, Glidewell & Patterson, 1996). Although we have been unable to obtain any solvent-free crystals of (I) which are suitable for single-crystal X-ray diffraction, we have obtained good quality crystals from methanol solutions for which microanalysis indicated the composition to be $3(I).2CH_3OH$. The structure analysis reported here both confirms and elucidates this unusual composition.

There are two types of molecule (I) in the triclinic unit cell of its methanol solvate, denoted *A* and *B*. Molecule *A* lies in a twofold general position, whereas molecule *B* lies across a centre of inversion. In addition, there are methanol molecules in general positions. Hence, the asymmetric unit consists of 1.5 molecules of (I) and one molecule of methanol, confirming the composition deduced from analytical data. In molecule *A* [Fig. 1(*a*)], there is an intramolecular O—H···O hydrogen bond (Table 3), characterized by the graph set *S*(8) (Etter, 1990; Etter, MacDonald & Bernstein, 1990; Bernstein, Davis, Shimoni & Chang, 1995), so commonly encountered in ferrocenediols (Glidewell *et al.*, 1994). In addition, the hydroxyl group of the methanol acts as a hydrogen-bond donor to the O1 atom of the ferrocenediol [Fig. 1(*a*)], so that the overall graph set for this aggregate is *S*(8)*D*, as found in many simple adducts of ferrocenediol (II) (Glidewell *et al.*, 1994).



(*a*)

(*b*)

Fig. 1. (*a*) A view of the methanol adduct of molecule *A* of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. (*b*) A view of molecule *B* of (I) lying about an inversion centre, with the atom-numbering scheme. Atom labels ending in an '*a*' refer to atoms at $(-x, 1-y, 1-z)$. Displacement ellipsoids are drawn at the 30% probability level.

Although the O1 atom acts as a bis-acceptor of hydrogen bonds, it is not a donor, while atom O8 is a donor, but not an acceptor, and none of the O atoms in the methoxy substituents (O34, O44, O54 and O64) act as acceptors of O—H···O hydrogen bonds. The centrosymmetric molecule *B* [Fig. 1(*b*)] does not participate in any O—H···O hydrogen bonds at all. Despite the presence within the asymmetric unit of seven independent methoxy groups, which are all potential hydrogen-bond acceptors, only two of the four hydroxyl groups in the asymmetric unit act as donors in O—H· · ·O hydrogen bonds. In this respect, the structure of this methanol solvate of (I) differs markedly from the structures of both unsolvated (II), which crystallizes as a dimer in which all the hydroxyl groups are involved in O—H· · ·O hydrogen bonds in an $R_4^4(8)$ motif (Ferguson *et al.*, 1993*a*), and the 1:1 methanol solvate of (II), where the hydrogen-bonded aggregate contains two molecules of each component and where all the hydroxyl groups participate in an $R_8^6(12)$ motif of O—H· · ·O hydrogen bonds (Ferguson *et al.*, 1993*b*). There are, however, two C—H· · ·O hydrogen bonds (Table 3). The phenyl C53—H53 bond in molecule *A* at (*x*, *y*, *z*) acts as donor towards the methoxy O44 atom in molecule *A* at (*x*, *y* − 1, *z*), so forming chains parallel to the **b** direction, and the ferrocenyl C75—H75 bond in molecule *B* at (*x*, *y*, *z*) acts as donor towards the O64 atom in molecule *A* at (−*x*, 1 − *y*, 1 − *z*).

In molecule *A*, the gross conformations of the two independent $Fe[C_5H_4C(OH)(C_6H_4OCH_3)_2]$ fragments are remarkably similar, as judged from the various O*n*—C*n*—C*n*1—C*n*2, O*n*—C*n*—C*n*1—C*n*5 and C*n*1—C*n*—C—C torsion angles (*n* = 1,2) [Fig. 1(*a*) and Table 2]; these conformations differ somewhat, however, from those adopted by molecule *B* [Fig. 1(*b*) and Table 2]. As a result of these conformations, there are a number of very short intramolecular H· · ·O contacts (Table 3). In molecule *A*, the cyclopentadienyl rings are midway between an eclipsed and staggered conformation, with a mean C1*m*—*Cg*1—*Cg*2—C2*m* (*m* = 1–5; *Cg*1 and *Cg*2 are the centroids of the C11–C15 and C21–C25 rings, respectively) torsion angle of −53.5 (5)° (the staggered and eclipsed conformation would have mean values of −36 and −72°, respectively); in molecule *B*, these rings are necessarily staggered. For each of the aryl rings, the methoxy substituent lies very close to the C_6H_4 plane and the *cis*-C—O—C angles are very much larger than the *trans*-C—O—C angles. This phenomenon has also been observed in both tris(4-methoxyphenyl)methanol (Ferguson *et al.*, 1996) and anisole (Seip & Seip, 1973). The C—O(H) bond lengths are very similar to those observed in compound (II) (Ferguson *et al.*, 1993*a*); the other interatomic distances are unexceptional. Examination of the structure with *PLATON* (Spek, 1995*a*) showed that there were no solvent-accessible voids in the crystal lattice.

Experimental

Compound (I) was prepared by reaction of 1,1′-dilithioferrocene with two equivalents of bis(4-methoxyphenyl)ketone, followed by acidification. This yielded (I) as a fine yellow–orange powder. NMR ($CDCl_3$): δ(H) 3.76 (*s*, 12H, CH_3), 3.97 (*m*, 4H) and 4.12 (*m*, 4H) (C_5H_4), 4.39 (*s*, *br*, 2H, OH), 6.72 and 7.19 (*AB*, 16H, C_6H_4); δ(C) 55.0 (*q*, CH_3), 68.1 (*d*), 69.2 (*d*) and 77.4 (*s*) (C_5H_4), 97.9 (*s*, COH), 112.5 (*d*), 128.1 (*d*), 139.9 (*s*) and 158.1 (*s*) (C_6H_4). Attempts to grow crystals suitable for single-crystal X-ray diffraction yielded, from most solvents employed, either fine powders or viscous oils. Suitable crystals were, however, obtained from methanol, which proved to have the composition 3(I).$2CH_3OH$. Analysis found: C 70.8, H 6.3%; $C_{122}H_{122}Fe_3O_{20}$ requires: C 70.6, H 5.9%. Crystals suitable for single-crystal diffraction were selected directly from the analytical sample.

Crystal data

$3[Fe(C_{20}H_{19}O_3)_2].2CH_4O$
$M_r = 2075.75$
Triclinic
$P\bar{1}$
$a = 11.505\,(2)$ Å
$b = 11.785\,(2)$ Å
$c = 19.950\,(3)$ Å
$\alpha = 74.93\,(2)°$
$\beta = 78.32\,(2)°$
$\gamma = 87.122\,(13)°$
$V = 2557.9\,(6)$ Å^3
$Z = 1$
$D_x = 1.348$ Mg m^{-3}
D_m not measured

Mo *K*α radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 8.22–13.18°$
$\mu = 0.493$ mm^{-1}
$T = 294\,(1)$ K
Rod
0.40 × 0.26 × 0.25 mm
Red

Data collection

Enraf–Nonius CAD-4 diffractometer
θ/2θ scans
Absorption correction: numerical by Gaussian integration from crystal shape
$T_{min} = 0.8680$, $T_{max} = 0.9078$
8911 measured reflections

8911 independent reflections
3120 observed reflections [$I > 2\sigma(I)$]
$\theta_{max} = 25°$
$h = -13 \rightarrow 13$
$k = 0 \rightarrow 13$
$l = -22 \rightarrow 23$
3 standard reflections
frequency: 120 min
intensity decay: 1.2%

Refinement

Refinement on F^2
$R(F) = 0.0686$
$wR(F^2) = 0.1270$
$S = 0.860$
8911 reflections
658 parameters
H atoms riding, with C—H 0.93–0.96 and O—H 0.82–0.90 Å
$w = 1/[\sigma^2(F_o^2) + (0.0306P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.306$ e Å^{-3}
$\Delta\rho_{min} = -0.344$ 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}
Fe1	0.21552 (7)	0.97478 (7)	0.22954 (4)	0.0403 (3)
O1	−0.0516 (3)	0.9836 (3)	0.1558 (2)	0.0395 (10)
C1	−0.0345 (5)	1.0834 (5)	0.1822 (3)	0.0354 (15)
C11	0.0467 (5)	1.0424 (5)	0.2349 (3)	0.0342 (15)
C12	0.1196 (5)	1.1122 (5)	0.2571 (3)	0.044 (2)
C13	0.1647 (5)	1.0414 (5)	0.3155 (3)	0.045 (2)
C14	0.1200 (5)	0.9284 (5)	0.3292 (3)	0.045 (2)
C15	0.0453 (5)	0.9272 (5)	0.2815 (3)	0.041 (2)

*Cg*1†	0.0993 (5)	1.0103 (5)	0.2836 (3)	–
O2	0.1336 (3)	0.8748 (3)	0.0849 (2)	0.0455 (11)
C2	0.2151 (5)	0.8019 (5)	0.1241 (3)	0.041 (2)
C21	0.2761 (5)	0.8763 (5)	0.1586 (3)	0.0367 (15)
C22	0.3053 (5)	0.9975 (5)	0.1265 (3)	0.042 (2)
C23	0.3745 (5)	1.0350 (5)	0.1666 (3)	0.047 (2)
C24	0.3925 (5)	0.9397 (6)	0.2224 (3)	0.051 (2)
C25	0.3305 (5)	0.8418 (6)	0.2181 (3)	0.053 (2)
*Cg*2†	0.3358 (5)	0.9381 (5)	0.1784 (3)	–
C31	−0.1571 (5)	1.1180 (5)	0.2197 (3)	0.039 (2)
C32	−0.2388 (5)	1.1712 (5)	0.1790 (3)	0.052 (2)
C33	−0.3509 (5)	1.2026 (5)	0.2098 (3)	0.051 (2)
C34	−0.3811 (5)	1.1823 (5)	0.2815 (3)	0.048 (2)
C35	−0.3021 (6)	1.1272 (5)	0.3235 (3)	0.059 (2)
C36	−0.1908 (5)	1.0959 (5)	0.2922 (3)	0.055 (2)
O34	−0.4874 (4)	1.2145 (4)	0.3175 (2)	0.0735 (14)
C37	−0.5772 (5)	1.2581 (5)	0.2788 (3)	0.071 (2)
C41	0.0176 (5)	1.1852 (5)	0.1201 (3)	0.036 (2)
C42	0.0591 (5)	1.1692 (5)	0.0536 (3)	0.045 (2)
C43	0.1091 (5)	1.2617 (6)	−0.0029 (3)	0.053 (2)
C44	0.1171 (6)	1.3711 (6)	0.0076 (4)	0.054 (2)
C45	0.0744 (5)	1.3886 (5)	0.0729 (4)	0.053 (2)
C46	0.0260 (5)	1.2982 (5)	0.1279 (3)	0.049 (2)
O44	0.1680 (4)	1.4673 (4)	−0.0440 (2)	0.0745 (14)
C47	0.2127 (7)	1.4518 (6)	−0.1120 (3)	0.107 (3)
C51	0.3055 (5)	0.7589 (5)	0.0680 (3)	0.0350 (15)
C52	0.2628 (5)	0.7064 (5)	0.0233 (3)	0.046 (2)
C53	0.3388 (5)	0.6658 (5)	−0.0281 (3)	0.047 (2)
C54	0.4603 (6)	0.6757 (5)	−0.0343 (3)	0.044 (2)
C55	0.5038 (5)	0.7271 (5)	0.0097 (3)	0.053 (2)
C56	0.4267 (5)	0.7681 (5)	0.0608 (3)	0.053 (2)
O54	0.5275 (4)	0.6347 (4)	−0.0891 (2)	0.0647 (13)
C57	0.6521 (6)	0.6266 (5)	−0.0914 (3)	0.074 (2)
C61	0.1499 (5)	0.6945 (5)	0.1772 (3)	0.042 (2)
C62	0.0279 (5)	0.6884 (5)	0.1958 (3)	0.047 (2)
C63	−0.0325 (5)	0.5892 (6)	0.2393 (3)	0.050 (2)
C64	0.0310 (6)	0.4901 (6)	0.2660 (3)	0.044 (2)
C65	0.1534 (6)	0.4957 (5)	0.2496 (3)	0.056 (2)
C66	0.2108 (6)	0.5945 (5)	0.2055 (3)	0.056 (2)
O64	−0.0161 (4)	0.3858 (4)	0.3081 (2)	0.0678 (14)
C67	−0.1412 (6)	0.3770 (6)	0.3276 (4)	0.088 (3)
Fe2	0	1/2	1/2	0.0525 (4)
O3	−0.2648 (3)	0.6155 (3)	0.5623 (2)	0.0697 (14)
C7	−0.2127 (5)	0.6926 (6)	0.4945 (3)	0.050 (2)
C71	−0.0826 (6)	0.6632 (5)	0.4774 (3)	0.046 (2)
C72	−0.0132 (6)	0.6377 (5)	0.4157 (3)	0.051 (2)
C73	0.1049 (6)	0.6218 (5)	0.4207 (4)	0.070 (2)
C74	0.1140 (6)	0.6339 (5)	0.4870 (5)	0.070 (2)
C75	0.0005 (6)	0.6590 (5)	0.5233 (4)	0.060 (2)
*Cg*3†	0.0247 (6)	0.6431 (5)	0.4648 (4)	–
C81	−0.2307 (6)	0.8198 (6)	0.5019 (3)	0.048 (2)
C82	−0.3413 (5)	0.8520 (6)	0.5341 (3)	0.051 (2)
C83	−0.3639 (6)	0.9652 (6)	0.5414 (3)	0.050 (2)
C84	−0.2747 (6)	1.0477 (6)	0.5147 (3)	0.051 (2)
C85	−0.1643 (6)	1.0186 (6)	0.4826 (3)	0.054 (2)
C86	−0.1441 (6)	0.9055 (6)	0.4766 (3)	0.051 (2)
O84	−0.2886 (4)	1.1632 (4)	0.5180 (2)	0.080 (2)
C87	−0.3949 (6)	1.1949 (6)	0.5576 (4)	0.101 (3)
C91	−0.2755 (6)	0.6780 (6)	0.4376 (4)	0.049 (2)
C92	−0.3443 (6)	0.5812 (6)	0.4463 (4)	0.075 (2)
C93	−0.3974 (7)	0.5628 (7)	0.3928 (6)	0.091 (3)
C94	−0.3795 (7)	0.6454 (9)	0.3282 (6)	0.092 (3)
C95	−0.3141 (7)	0.7446 (7)	0.3184 (4)	0.079 (2)
C96	−0.2608 (6)	0.7601 (6)	0.3721 (4)	0.062 (2)
O94	−0.4214 (6)	0.6397 (6)	0.2682 (4)	0.136 (3)
C97	−0.4814 (8)	0.5398 (9)	0.2723 (6)	0.177 (5)
O8	−0.1964 (4)	1.0022 (4)	0.0582 (2)	0.0672 (13)
C8	−0.3186 (6)	0.9735 (6)	0.0819 (4)	0.096 (3)

† *Cg*1, *Cg*2 and *Cg*3 are the centroids of rings C11–C15, C21–C25 and C71–C75, respectively.

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

Fe1—*Cg*1	1.650 (5)	C54—O54	1.387 (6)
Fe1—*Cg*2	1.655 (5)	O54—C57	1.424 (6)
O1—C1	1.444 (6)	C64—O64	1.363 (6)
C1—C11	1.517 (7)	O64—C67	1.415 (7)
C1—C31	1.547 (7)	Fe2—*Cg*3	1.664 (6)
C1—C41	1.527 (7)	O3—C7	1.451 (6)
O2—C2	1.448 (6)	C7—C71	1.510 (7)
C2—C21	1.518 (7)	C7—C81	1.543 (8)
C2—C51	1.537 (7)	C7—C91	1.512 (8)
C2—C61	1.538 (7)	C84—O84	1.379 (7)
C34—O34	1.376 (6)	O84—C87	1.406 (6)
O34—C37	1.412 (6)	C94—O94	1.395 (9)
C44—O44	1.380 (7)	O94—C97	1.371 (9)
O44—C47	1.406 (7)	O8—C8	1.418 (6)
*Cg*1—Fe1—*Cg*2	177.9 (2)	O54—C54—C55	125.8 (6)
O1—C1—C11	106.3 (4)	O54—C54—C53	114.0 (6)
O1—C1—C41	109.2 (4)	C54—O54—C57	116.3 (5)
C11—C1—C41	113.0 (5)	O64—C64—C65	115.6 (6)
O1—C1—C31	107.8 (4)	O64—C64—C63	126.1 (6)
C11—C1—C31	110.3 (5)	C64—O64—C67	117.5 (5)
C31—C1—C41	110.0 (5)	*Cg*3^{i}—Fe2—*Cg*3	180
O2—C2—C21	109.2 (4)	O3—C7—C71	108.3 (5)
O2—C2—C51	104.7 (4)	O3—C7—C91	110.3 (5)
C21—C2—C51	110.5 (5)	C71—C7—C91	110.9 (5)
O2—C2—C61	110.3 (5)	O3—C7—C81	107.1 (5)
C21—C2—C61	113.3 (5)	C71—C7—C81	111.4 (5)
C51—C2—C61	108.5 (4)	C81—C7—C91	108.8 (5)
O34—C34—C33	124.6 (6)	O84—C84—C85	115.6 (7)
O34—C34—C35	115.2 (6)	O84—C84—C83	123.4 (6)
C34—O34—C37	117.9 (5)	C84—O84—C87	118.1 (6)
O44—C44—C43	124.4 (7)	O94—C94—C95	113.5 (10)
C44—C45—C46	120.7 (6)	O94—C94—C93	126.6 (10)
C44—O44—C47	117.4 (6)	C94—O94—C97	117.0 (9)
O1—C1—C11—C12	157.3 (5)	O2—C2—C61—C62	−15.3 (7)
O1—C1—C11—C15	−35.6 (7)	C21—C2—C61—C62	107.4 (6)
O2—C2—C21—C25	157.1 (5)	C63—C64—O64—C67	−0.9 (9)
O2—C2—C21—C22	−34.0 (7)	O3—C7—C71—C72	128.5 (6)
C11—C1—C31—C32	172.3 (5)	O3—C7—C71—C75	−53.7 (8)
C33—C34—O34—C37	8.5 (9)	C71—C7—C81—C82	−164.2 (5)
O1—C1—C41—C42	−10.8 (7)	C83—C84—O84—C87	7.3 (9)
C11—C1—C41—C42	107.3 (6)	O3—C7—C91—C92	−18.3 (8)
C43—C44—O44—C47	1.1 (9)	C71—C7—C91—C92	101.7 (7)
C21—C2—C51—C52	−169.5 (5)	C93—C94—O94—C97	−3.5 (13)
C53—C54—O54—C57	−171.0 (5)		

Symmetry code: (i) $-x, 1-y, 1-z$.

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O1	0.82	1.97	2.764 (5)	164
O8—H8···O1	0.82	1.99	2.769 (5)	158
C42—H42···O1	0.93	2.36	2.734 (7)	104
C53—H53···O44^{i}	0.93	2.51	3.246 (8)	136
C62—H62···O2	0.93	2.45	2.802 (7)	102
C75—H75···O64^{ii}	0.93	2.48	3.307 (8)	148
C92—H92···O3	0.93	2.42	2.781 (8)	103

Symmetry codes: (i) $x, y-1, z$; (ii) $-x, 1-y, 1-z$.

Data collection: *CAD-4-PC* (Enraf–Nonius, 1992). Cell refinement: *SET*4 and *CELDIM* in *CAD-4-PC*. Data reduction: *DATRD*2 in *NRCVAX*94 (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *NRCVAX*94 and *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *NRCVAX*94, *PLATON* (Spek, 1995*a*) and *PLUTON* (Spek 1995*b*). Software used to prepare material for publication: *NRCVAX*94, *SHELXL*93 and *WordPerfect* (macro *PREPCIF*).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1403). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Pentaammine-2κ⁵*N*-(μ-4,4′-bipyridine-1κ*N*:2κ*N*′)(2,2′-bipyridine-1κ²*N*,*N*′)-(2,2′:6′,2″-terpyridine-1κ³*N*,*N*′,*N*″)diruthenium Tetrakis(hexafluorophosphate) Acetonitrile Solvate

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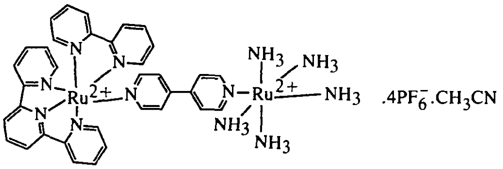
Abstract

In the title compound, $[Ru_2(C_{10}H_8N_2)_2(C_{15}H_{11}N_3)(NH_3)_5](PF_6)_4.CH_3CN$, the bridging Ru—N bond length in the Ru(2,2′-bipyridine)(2,2′:6′,2″-terpyridine)(4,4′-bipyridine) moiety is 2.112 (7) Å, whereas that in the $Ru(NH_3)_5$(4,4′-bipyridine) moiety is 2.052 (7) Å. The difference arises from the fact that the $[Ru^{II}(NH_3)_5]^{2+}$ group is a stronger π-donor than the $[Ru^{II}$(2,2′-bipyridine)(2,2′:6′,2″-terpyridine)$]^{2+}$ moiety.

Comment

Ruthenium complexes of the tridentate 2,2′:6′2″-terpyridine (terpy) ligand and of the bidentate 2,2′-bipyridine (bpy) ligand are attractive as potential photocatalysts (Constable, 1986; Hecker, Gushurst & McMillin, 1991; Petersen, Morgan, Hsu, Billadeau & Ronco, 1991), powerful electrocatalysts for oxidation of organic substrates (Moyer, Thompson & Meyer, 1980; Thompson & Meyer, 1982; Binstead & Meyer, 1987), effective agents for DNA cleavage (Grover, Gupta, Singh & Thorp, 1992) and building blocks for supramolecular species (Collin *et al.*, 1991). In the course of our studies of mono- and dinuclear complexes (Fagalde & Katz, 1993, 1995) derived from the photosensitizing $[Ru^{II}$(terpy)(bpy)$]^{2+}$ unit, we have obtained crystals of the PF_6^- salt of the [(terpy)(bpy)Ru^{II}(μ-4,4′-bpy)$Ru^{II}(NH_3)_5]^{4+}$ cation (where 4,4′-bpy is 4,4′-bipyridine), (1). These systems are important in mixed-valence chemistry (Creutz, 1983; Meyer, 1978) and structural data are necessary in the reorganizational energy calculations for intramolecular electron transfers.



(I)

An *ORTEP*III (Burnett & Johnson, 1996) drawing of (1) is shown in Fig. 1. The left-hand side of the molecule consists of an Ru atom coordinated to a 2,2′-bipyridine ligand, a 2,2′:6′,2″-terpyridine ligand and a 4,4′-bipyridine ligand which bridges the [Ru(bpy)(terpy)$]^{2+}$ and $[Ru(NH_3)_5]^{2+}$ metal centers. Both Ru atoms are in the +2 oxidation state. The asymmetric unit also contains four hexafluorophosphate anions, one of which is disordered. There is also one acetonitrile molecule of crystallization in the asymmetric unit which is also disordered. The acetonitrile molecule is disordered over at least two positions and displays weak hydrogen bonding with the ammine ligands and the anions in both positions. The hexafluorophosphate anions are also hydrogen bonded to the coordinated ammine ligands. The bond lengths and angles within the bipyridine and terpyridine ligands are normal. The [Ru(bpy)(terpy)$]^{2+}$—N(4,4′-bpy) bond length of 2.112 (7) Å is very similar to that observed in [Ru(terpy)(bpy)(py)$]^{2+}$ of 2.114 (6) Å (Hecker, Fanwick & McMillin, 1991). The $[Ru(NH_3)_5]^{2+}$—N(4,4′-bpy) bond length of 2.052 (7) Å is significantly longer than the Ru—N(pz) bond length (pz is pyrazine) of 2.006 (6) Å observed in