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(Diethylenetriamine-κ^3N)(η^5-pentamethylcyclopentadienyl)iridium(III) bis(trifluoromethanesulfonate)

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The title compound, $[Ir(\eta^5\text{-}C_5Me_5)(dien\text{-}\kappa^3N)](CF_3SO_3)_2$ (dien is diethylenetriamine) or $[Ir(C_{10}H_{15})(C_4H_{13}N_3)](CF_3SO_3)_2$, contains a half-sandwich $(\eta^5\text{-}C_5Me_5)Ir^{III}$ fragment coordinated in a facial manner by the N atoms of a dien ligand. N—H···O hydrogen bonds to the trifluoromethanesulfonate counter-anions link the organometallic cations into a chiral polymeric network.

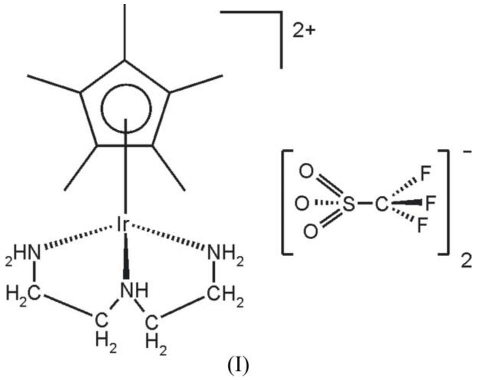
Key indicators

Single-crystal X-ray study
T = 292 K
Mean σ(C–C) = 0.015 Å
R factor = 0.027
wR factor = 0.064
Data-to-parameter ratio = 8.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Many (pentamethylcyclopentadienyl)iridium(III) complexes with bidentate aromatic *N*-donor ligands have been structurally characterized, *e.g.* $[(\eta^5\text{-}C_5Me_5)IrCl(bpy)]X$ (bpy is bipyridine), with X = Cl (Youinou & Ziessel, 1989) and ClO_4^- (Dadci *et al.*, 1995). In contrast, perusal of the Cambridge Structural Database (Version 5.27, December 2006; Allen, 2002) indicates that in each case only one example has been reported for an $(\eta^5\text{-}C_5Me_5)Ir^{III}$ complex containing a bidentate or tridentate ligand with exclusively amino *N*-donor atoms. The relevant compounds are $[(\eta^5\text{-}C_5Me_5)Ir(H_2O)(1,2\text{-diaminocyclohexane-}\kappa^2N,N')](ClO_4)_2\cdot H_2O$ (Poth *et al.*, 2001) and $[(\eta^5\text{-}C_5Me_5)Ir(1,4,7\text{-triazocyclononane-}\kappa^3N,N',N'')](PF_6)_2\cdot CH_3NO_2$ (Grant *et al.*, 2005). During the course of our continuing studies on organometallic half-sandwich complexes (Frodl *et al.*, 2002; Gencaslan & Sheldrick, 2005; Herebian & Sheldrick, 2002; Scharwitz *et al.*, 2007*a*,*b*), we have recently prepared the title compound $[Ir(\eta^5\text{-}C_5Me_5)(dien\text{-}\kappa^3N)](CF_3SO_3)_2$ (dien is diethylenetriamine), (I), and the lack of structural data on $(\eta^5\text{-}C_5Me_5)Ir^{III}$ complexes with tridentate amino ligands prompted us to determine the crystal structure.



(I)

The molecular structure of the cation of (I) is depicted in Fig. 1. The Ir—C14 distance of 2.129 (8) Å is somewhat shorter than the other four Ir—C distances (Table 1), which lie in the range 2.162 (9)–2.176 (7) Å. Whereas a twist λ conformation is observed for the first chelate ring (N1 and N2 as

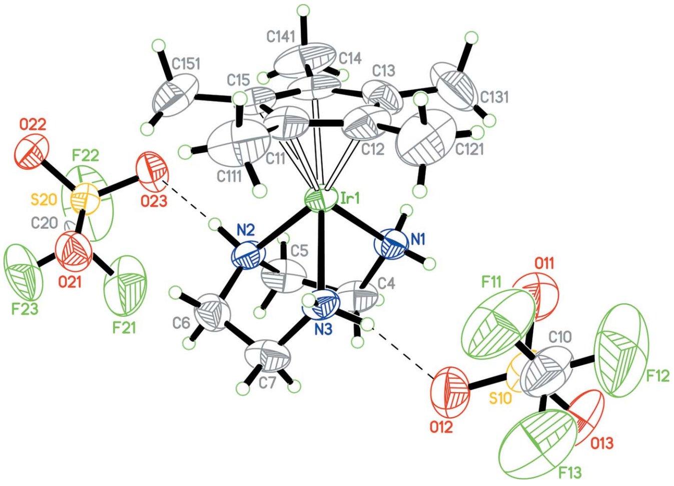


Figure 1

The asymmetric unit of compound (I). Displacement ellipsoids are drawn at the 50% probability level.

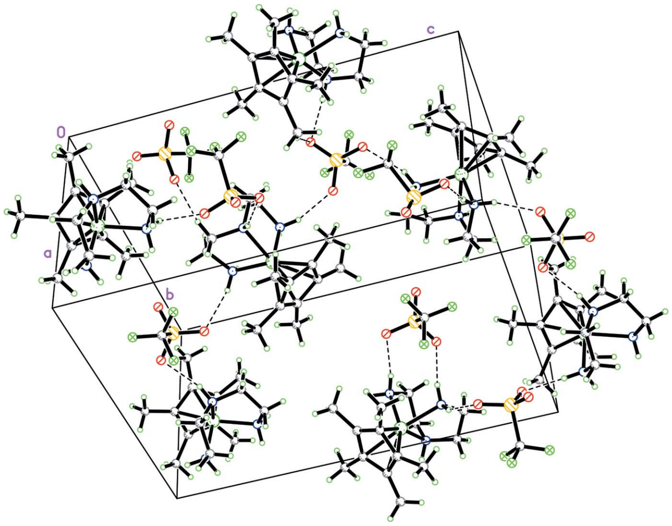


Figure 2

A projection of the structure of (I), with hydrogen bonds shown as dashed lines.

donor atoms), an envelope conformation is adopted by the second ring (N2 and N3 as donor atoms). Atoms C4 and C5 are displaced by −0.288 and 0.327 Å, respectively, from the plane through Ir1, N1 and N2 in the first case. A displacement of 0.530 (6) Å from the mean plane through Ir1, N2, C7 and N3 is observed for the flap atom C6 in the second case. The Ir1—N distances of 2.140 (6), 2.137 (7) and 2.139 (6) Å are identical within the precision of the analysis. All three N atoms participate in N—H···O hydrogen bonds to trifluoromethanesulfonate counter-anions, as depicted in Fig. 2 and listed in Table 2.

Experimental

Ag(CF_3SO_3) (51.4 mg, 0.2 mmol) were added to a solution of [(η^5-C_5Me_5)$IrCl_2$]$_2$ (39.8 mg, 0.05 mmol) in acetone (10 ml) and stirred at room temperature for 30 min. After centrifugation of the resulting AgCl and solvent removal, the residue was treated with 10.8 µl diethylenetriamine (0.1 mmol) in CH_3OH/CH_2Cl_2 (10 ml, 1:1). The reaction solution was heated for 2 h at 348 K and the solvent subsequently removed to afford (I), which was dissolved in methanol (3 ml) and reprecipitated with diethyl ether prior to drying in vacuum. Elemental analysis found: C 26.4, H 3.9, N 6.2, S 8.9%; calculated for $C_{16}H_{28}F_6IrN_3O_6S_2$: C 26.4, H 3.9, N 5.8, S 8.8%. FAB–MS on a VG Autospec instrument (*m/z*): 580 (54%) [$M - CF_3SO_3$]$^+$, 430 (100%) [$M - 2CF_3SO_3$]$^+$.

Crystal data

[Ir($C_{10}H_{15}$)($C_4H_{13}N_3$)](CF_3SO_3)$_2$
$M_r = 728.73$
Orthorhombic, $P2_12_12_1$
$a = 10.244$ (2) Å
$b = 13.733$ (3) Å
$c = 17.869$ (4) Å
$V = 2513.8$ (9) Å^3
$Z = 4$
$D_x = 1.926$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 5.56$ mm^{-1}
$T = 292$ (2) K
Block, colourless
0.55 × 0.47 × 0.37 mm

Data collection

Siemens P4 4-circle diffractometer
ω scans
Absorption correction: ψ scan
(North *et al.* (1968)
$T_{\min} = 0.057$, $T_{\max} = 0.130$
2511 measured reflections
2511 independent reflections
2335 reflections with $I > 2\sigma(I)$
$\theta_{\max} = 25.0°$
3 standard reflections
every 100 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.064$
$S = 1.05$
2511 reflections
314 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0389P)^2 + 0.5443P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.65$ e Å^{-3}
$\Delta\rho_{\min} = -0.84$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0028 (2)
Absolute structure: Flack (1983)
Flack parameter: 0.006 (13)

Table 1

Selected bond lengths (Å).

Ir1—C14	2.129 (8)	Ir1—C13	2.162 (9)
Ir1—N2	2.137 (7)	Ir1—C12	2.165 (9)
Ir1—N3	2.139 (6)	Ir1—C15	2.175 (9)
Ir1—N1	2.140 (6)	Ir1—C11	2.176 (7)

Table 2

Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H12···O11^{i}	0.90	2.17	3.062 (14)	171
N2—H2···O23^{ii}	0.91	2.24	3.080 (10)	154
N3—H31···O12^{i}	0.90	2.09	2.943 (11)	157
N3—H32···O21^{iii}	0.90	2.20	3.036 (10)	155
N1—H11···O22^{iv}	0.90	2.08	2.947 (9)	162

Symmetry codes: (i) $-x+1, y-\frac{1}{2}, -z+\frac{3}{2}$; (ii) $x-\frac{1}{2}, -y+\frac{3}{2}, -z+1$; (iii) $-x+\frac{1}{2}, -y+1, z+\frac{1}{2}$; (iv) $x, y, z+1$.

The H atoms of the cation were constrained to idealized positions and refined using a riding model, with C—H = 0.97 Å for the methylene C atoms and 0.96 Å for the methyl groups, and N—H = 0.91 Å for N2 and 0.90Å for N1 and N3 [U_{iso}(H) = 1.2U_{eq}(C) for methylene C atoms, 1.5U_{eq}(C111–C151) and 1.2U_{eq}(N)].

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Data collection: *R3m/V* (Siemens, 1989); cell refinement: *R3m/V*; data reduction: *XDISK* (Siemens, 1989); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 1995); software used to prepare material for publication: *SHELXL97*.

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.

Dadci, L., Elias, H., Frey, V., Horning, A., Koelle, U., Merbach, A. E., Paulus, H. & Schneider, J. S. (1995). *Inorg. Chem.* **34**, 306–315.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Frodl, A., Herebian, D. & Sheldrick, W. S. (2002). *J. Chem. Soc. Dalton Trans.* pp. 3664–3673.

Gencaslan, S. & Sheldrick, W. S. (2005). *Eur. J. Inorg. Chem.* pp. 3840–3849.

Grant, G. J., Lee, J. P., Helm, M. L., VanDerveer, D. G., Pennington, W. T., Harris, J. L., Mehne, L. F. & Klinger, D. W. (2005). *J. Organomet. Chem.* **690**, 629–639.

Herebian, D. & Sheldrick, W. S. (2002). *J. Chem. Soc. Dalton Trans.* pp. 966–974.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Poth, T., Paulus, H., Elias, H., Ducker-Benfer, C. & van Eldik, R. (2001). *Eur. J. Inorg. Chem.* pp. 1361–1369.

Scharwitz, M., Almsick, T. van & Sheldrick, W. S. (2007*a*). *Acta Cryst.* E**63**, m105–m107.

Scharwitz, M., Almsick, T. van & Sheldrick, W. S. (2007*b*). *Acta Cryst.* E**63**, m230–m232.

Sheldrick, G. M. (1995). *SHELXTL*. Release 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Siemens (1989). *R3m/V* (Version 3.2) and *XDISK* (Version 3.11). Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Youinou, M.-T. & Ziessel, R. (1989). *J. Organomet. Chem.* **363**, 197–208.

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