

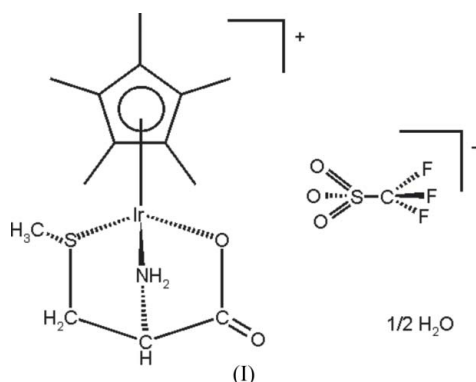
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Key indicators

Single-crystal X-ray study
 $T = 292$ K
Mean $\sigma(\text{C}-\text{C}) = 0.016$ Å
H-atom completeness 96%
Disorder in solvent or counterion
 R factor = 0.032
 wR factor = 0.080
Data-to-parameter ratio = 10.5For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.**(*S*-Methylcysteinato)(η^5 -pentamethylcyclopenta-
dienyl)iridium(III) trifluoromethanesulfonate
hemihydrate**The cation of the title compound, $[\text{Ir}(\text{C}_{10}\text{H}_{15})\text{-(C}_4\text{H}_8\text{NO}_2\text{S)}](\text{CF}_3\text{SO}_3)\cdot 0.5\text{H}_2\text{O}$, contains a half-sandwich $[\text{Ir}(\text{C}_5\text{Me}_5)]^{2+}$ fragment, the Ir^{III} atom of which is coordinated by the tridentate *S*-methylcysteinate ligand (*S*-MecysO) in a κ^3N,O,S manner. An R_{Ir} configuration is observed for the transition metal and an S_{S} configuration for the chiral thioether S atom.Received 24 October 2006
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Comment

α -Amino acids with coordinating side chains can function as tridentate ligands towards the half-sandwich organometallic fragments $(\text{C}_5\text{Me}_5)M$ ($M = \text{Ru}, \text{Co}, \text{Rh}$ or Ir), leading to the formation of *N,O,N*-(*L*-histidine) (Krämer *et al.*, 1990; Sheldrick, Hauck & Korn, 1994), *N,O,O*-(*L*-aspartic acid) (Krämer *et al.*, 1990; Bergs *et al.*, 1993; Sheldrick, Hauck & Korn, 1994) and *N,O,S*-chelates with *L*-methionine, *L*-methylcysteine and *L*-penicillamine (Sheldrick, Hauck & Korn, 1994; Sheldrick & Gleichmann, 1994; Zhou *et al.*, 1994). The crystal structure determinations of $[(\text{C}_5\text{Me}_5)\text{Co}(\text{H-met-O})](\text{FeCl}_4)$ (*H-met-OH* = *L*-methionine) and $[(\text{C}_5\text{Me}_5)\text{Co}(\text{S-Mecys-O})\text{CoCl}_3]$ (Sheldrick, Hauck & Korn, 1994) have established differing chiralities for the coordinating thioether S atoms. An R_{S} configuration is observed in the former case and an S_{S} configuration in the latter complex, whose *S*-Mecys-O ligand is tetradentate. The chiralities of the S and metal atoms in such complexes are assigned in accordance with the Cahn–Ingold–Prelog rules and the IUPAC recommendations for pseudo-tetrahedral organometallic complexes, *i.e.* by giving the pentamethylcyclopentadienyl ligand the highest priority. Whereas the S–Co–O and O–Co–N angles are similar in both complexes, a marked narrowing of the S–Co–N angles from 93.4 (2) to 85.2 (5)° is observed on going from the six-membered ring of the *H-met-O* complex to the more strained five-membered ring of the *S-Mecys-O* complex.



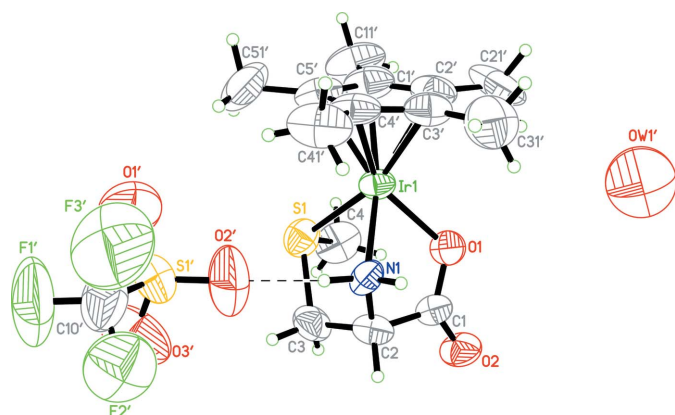


Figure 1
The asymmetric unit of (I). Displacement ellipsoids are drawn at the 50% probability level. The dashed line indicates a hydrogen bond.

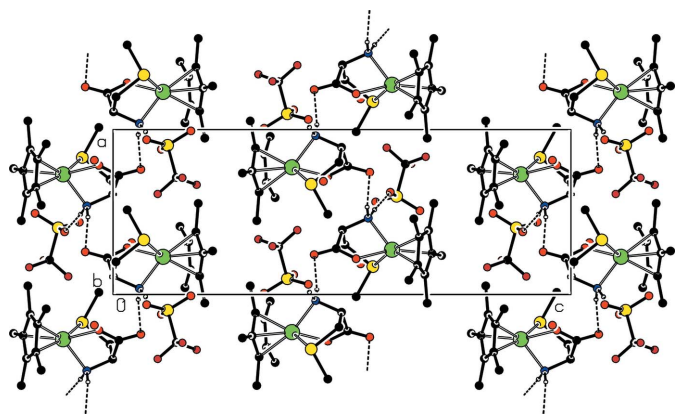


Figure 2
A projection of the crystal structure along the *b* axis, showing the hydrogen bonds as dashed lines. H atoms not involved in hydrogen bonding have been omitted for clarity.

We have determined the structure of the title compound, (I), to establish the S-atom configuration for a tridentate *S*-Mecys-O ligand. As depicted in Fig. 1, this once again adopts an S_S configuration, presumably to avoid a relatively close intramolecular contact between the S lone pair and the coordinating carboxylate O atom. Both five-membered chelate rings exhibit envelope conformations with atom N1 in the flap position.

As a result of the markedly longer Ir1–N1 and Ir1–S1 distances of 2.096 (7) and 2.372 (3) Å, respectively, in (I) compared with the analogous Co–N1 and Co1–S1 distances of 1.97 (1) and 2.270 (5) Å, respectively, in [(C₅Me₅)Co(*S*-Mecys-O)CoCl₃] (Sheldrick, Hauck & Korn, 1994), the N1–M–S1 angle narrows to 81.1 (2)° for *M* = Ir compared with 85.0 (4)° for *M* = Co. This is also the case for the N1–M–O1 and S1–M–O1 angles, whose values of 76.1 (3) and 85.0 (2)° for *M* = Ir are on average 6.4° smaller than for *M* = Rh. A concomitant increase in the bond angles at S1 from 95.3 (5) (for *M* = Co) to 99.0 (4)° for Ir1–S1–C3, and from 105.4 (6) (for *M* = Co) to 108.9 (5)° for Ir1–S1–C4, compensates for the narrower N1–Ir1–S1 angle.

The amino function of (I) participates in two intermolecular hydrogen bonds, delineating infinite chains along the *a* axis (Table 1 and Fig. 2).

Experimental

Ag(CF₃SO₃) (102.7 mg, 0.4 mmol) was added to a solution of [(C₅Me₅)IrCl₂]₂ (79.7 mg, 0.1 mmol) in acetone (10 ml). Following stirring at room temperature for 30 min and centrifugation of the resulting AgCl, the solvent was removed under vacuum and the remaining solid treated with *S*-methylcysteine (27.0 mg, 0.2 mmol) in a CH₃OH–CH₂Cl₂ (1:1, 10 ml) mixture. After heating for 2 h at 348 K and solvent removal, the product, (I), was dissolved in methanol–H₂O (1:1, 3 ml), precipitated with diethyl ether and dried under vacuum (yield 65%). Elemental analysis for C₁₅H₂₃F₃IrNO₅S₂ (*M*_r = 610.70): found C 29.7, H 3.8, N 2.3, S 11.0%; calculated C 29.5, H 3.8, N 2.3, S 10.5%; FAB-MS: *m/z* (%) 462 (100) [*M* – CF₃SO₃]⁺. Single crystals suitable for X-ray analysis were grown by slow evaporation of an aqueous solution of (I).

Crystal data

[Ir(C₁₀H₁₅)(C₄H₈NO₂S)]-
(CF₃SO₃)·0.5H₂O
*M*_r = 619.67
Orthorhombic, *P*2₁2₁2₁
a = 8.510 (5) Å
b = 10.728 (3) Å
c = 23.664 (4) Å
V = 2160.4 (14) Å³

Z = 4
*D*_x = 1.905 Mg m⁻³
Mo *K*α radiation
μ = 6.43 mm⁻¹
T = 292 (2) K
Prism, yellow
0.49 × 0.28 × 0.23 mm

Data collection

Siemens *P*4 four-circle
diffractometer
ω scans
Absorption correction: *ψ* scan
(*XP*REP in *SHELXTL*;
Sheldrick, 1995)
*T*_{min} = 0.130, *T*_{max} = 0.230
2865 measured reflections

2677 independent reflections
2487 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.030
*θ*_{max} = 25.0°
3 standard reflections
every 100 reflections
intensity decay: 2%

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.032
wR (*F*²) = 0.080
S = 1.06
2677 reflections
256 parameters
H-atom parameters constrained

w = 1/[σ²(*F*_o²) + (0.0479*P*)²
+ 2.2565*P*]
where *P* = (*F*_o² + 2*F*_c²)/3
(Δ/σ)_{max} = 0.001
Δρ_{max} = 1.37 e Å⁻³
Δρ_{min} = -0.83 e Å⁻³
Absolute structure: Flack (1983),
498 Friedel pairs
Flack parameter: -0.007 (16)

Table 1

Hydrogen-bond geometry (Å, °).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
N1–H11...O2 ⁱ	0.90	2.12	2.984 (11)	160
N1–H12...O2 ⁱⁱ	0.90	1.95	2.846 (13)	176

Symmetry codes: (i) *x* – ½, –*y* + ½, –*z*; (ii) *x* – 1, *y* + 1, *z*.

The H atoms of the cation were constrained to idealized positions and refined using a riding model, with C–H = 0.98 Å for atom C2, 0.97 Å for atom C3, and 0.96 Å for atom C4 and the C₅Me₅ methyl C atoms C1'–C5', and N–H = 0.90 Å for atom N1, with *U*_{iso}(H) = 1.2*U*_{eq}(C2, C3), 1.5*U*_{eq}(C4, C1'–C5') or 1.2*U*_{eq}(N1). The *R* config-

uration of the *S*-methylcysteine C α atom is known for the natural amino acid and was assigned to C2. It was confirmed by the Flack (1983) parameter $x = 0.01$ (2). The site-occupation factor of the water atom OW1' refined to a value close to 0.5 and was subsequently fixed at half occupancy. The highest peak in the final difference synthesis is 0.90 Å from Ir1.

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: *SHELXTL-Plus* (Sheldrick, 1995); software used to prepare material for publication: *SHELXL97*.

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