Synthesis, crystal structure, and enantioseparation of a homometallic, chiral cluster [$Ru_3(CO)_9${1,2-μ-FcC(CH_3) = NNC(S)NHCH_3}]

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Reaction of $Ru_3(CO)_{12}$ with the thio-Schiff base ligand acetylferrocenyl-thiosemicarbazone provides a one-step synthesis of the chiral cluster [$Ru_3(CO)_9${1,2-μ-FcC(CH_3) = NNC(S)NHCH_3}] as a racemic mixture. One molecule of thiosemicarbazone was consumed in the cluster formation process, in which the ligand was deprotonated and acted as a bidentate N, S donor as well as bridging. The title cluster has been characterised by NMR, IR, HPLC and an X-ray structure determination.

Keywords: homometallic chiral cluster, enantioseparation, acetylferrocenyl-thiosemicarbazone, X-ray structure

In the framework of a chiral cluster, the asymmetric induction generally originates from the central or planar chirality of a P or N ligand.[1-2] This paper investigates the substitution of carbonyls of the $Ru_3(CO)_{12}$ cluster by a bidentate N, S donor ligand, acetylferrocenyl-thiosemicarbazone.[3] This ligand reacts with $Ru_3(CO)_{12}$ at room temperature in THF for 10 hours to give, with retention of the ruthenium metal triangle, the chiral cluster [$Ru_3(CO)_9${1,2-μ-FcC(CH_3) = NNC(S)NHCH_3}], as a racemic mixture. The triruthenium cluster enantiomers can be separated directly without derivatisation by HPLC on a chiral stationary phase (CSP).[4-5]

The core of the cluster molecule is presented in Fig. 1 and selected bond distances and angles are listed in Table 1. The Ru3 triangle is unsymmetrical; each Ru atom is attached to corresponding carbonyl ligands. The ligand is deprotonated and the –NNCS– ligand system exhibits both chelating (through N1 and S1 to Ru1, forming a five-membered chelate ring) and edge bridging (through μ_2-S1 to Ru1 and Ru2). The edge bridge plays an important role in the retention of the metal triangle. Thus the Ru(1)–Ru(2) bond length, 2.842 Å, is longest of three Ru–Ru bond lengths. The two C-N distances C(6)–N(1) and C(8)–N(2) are respectively 1.293 Å and 1.295 Å, while the C(8)–S(1) distance is 1.771 Å. These distances are intermediate between single and double bond lengths, which suggests some π-electron delocalisation over the five-membered chelate ring.

The IR spectrum of the cluster shows intense terminal carbonyl absorption bands in the range 1934–2089. The ^{1}H and ^{13}C NMR results for the cluster were obtained in $CDCl_3$ solution. Due to the chirality and the π-electron delocalisation of the title cluster, the four nuclei of the substituted Cp ring have different chemical shifts, each nuclear signal is split by coupling with all the other nuclei, thus each nucleus gives the quintet pattern shown at δ = 4.59, 4.61, 4.65, 5.03. There is an upfield shift of the broad NH signal to δ = 4.83. The ^{13}C NMR spectra of the studied compound show eight resonances in the carbonyl region at δ = 185.66, 190.45, 193.42, 197.49, 199.00, 203.74, 204.64, and 204.86.

The structures of the pair of structurally related enantiomers are shown in Scheme 1. The enantioseparation (Fig. 2) of the title chiral cluster was successfully achieved on a cellulose tris-(3, 5-dimethyl-phenylcarbamate) chiral stationary phase (CDMPC–CSP) by HPLC. The presence of the first peak is due to the decomposition of the product and the last two peaks are eluted for the pure title cluster, which we consider to be definitive evidence for the existence of two enantiomers for the cluster.

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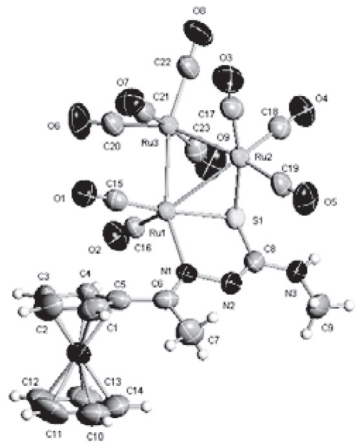
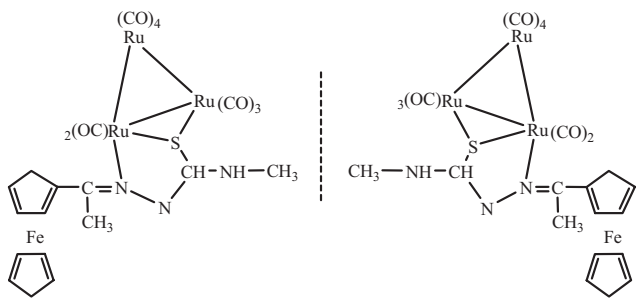


Fig.1 Crystal structure of the title cluster.

Table 1 Selected bond distances (**Å**) and angles (deg) of the title cluster

Ru(1)–Ru(2)	2.8416(7)	Ru(2)–Ru(3)	2.8134(7)
Ru(1)–Ru(3)	2.7883(7)	Ru(1)–N(1)	2.190(4)
Ru(1)–S(1)	2.3446(14)	Ru(2)–S(1)	2.4025(15)
N(1)–C(6)	1.293(7)	N(2)–C(8)	1.295(7)
N(1)–N(2)	1.397(6)	S(1)–C(8)	1.771(6)
C(16)–Ru(1)–N(1)	104.3(2)	C(15)–Ru(1)–N(1)	100.3(2)
C(16)–Ru(1)–S(1)	96.13(18)	C(15)–Ru(1)–S(1)	171.08(18)
N(1)–Ru(1)–S(1)	80.56(12)	C(16)–Ru(1)–Ru(3)	89.14(17)
C(15)–Ru(1)–Ru(3)	92.54(17)	N(1)–Ru(1)–Ru(3)	160.87(11)
S(1)–Ru(1)–Ru(3)	84.56(4)	N(1)–Ru(1)–Ru(2)	101.29(11)
S(1)–Ru(1)–Ru(2)	54.17(4)	Ru(3)–Ru(1)–Ru(2)	59.954(15)



Scheme 1 Structures of the pair of chiral clusters.

Experimental

All the reagents used in the synthesis were commercially available and were used without further purification. The FcC(Me) = NNC(S)NHMe[3] complexes were prepared according to the literature method.

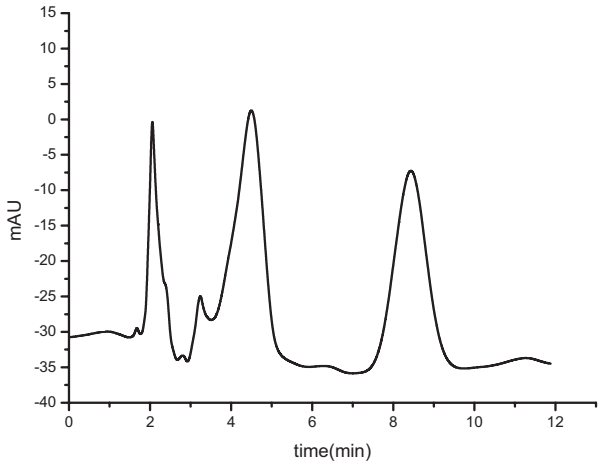


Fig. 3 Optimal chromatogram of the cluster enantiomers on (150 × 4.6 mm i.d.) cellulose tris (3,5- dimethylphenylcarbamate) coated amino-propylated silica gel column. Mobile phase: isopropanol: methanol : hexanol (2 : 3 : 95, v/v), flow-rate: 1.0 ml min^{-1}; UV detector: 231 nm, temperature: 25°C.

IR spectra were recorded on a Nicolet FT-10DX spectrometer with the samples in the form of KBr pellets. The NMR spectra were recorded on a Bruker AM400 spectrometer.

The sample was dissolved in mobile phase, cellulose tris (3,5-dimethylphenylcarbamate) was coated on aminopropylated silica gel with a coating amount of 15% (w/w). The chiral stationary phase prepared was packed into a stainless steel column (150 × 4.6 mm) by the conventional high pressure slurry-packing procedure.

Preparation of the title cluster

A 250-ml 3-neck flask with a condenser and a gas inlet was charged with $Ru_3(CO)_{12}$ (200 mg, 0.313 mmol), FcC(Me) = NNC(S)NHMe (93.9 mg, 0.313 mmol), and 40 ml of THF. The reaction mixture was reacted for 10 h under a slow dinitrogen sweep. The solvent was removed under reduced pressure and the residual solid was purified by column chromatography on silica gel with petroleum (60–90)/CH_2Cl_2 6 : 1. The second orange band which includes the product was collected, and the solvent was removed under reduced pressure. Crystals suitable for X-ray diffraction analysis were obtained by recrystallisation from hexane–CH_2Cl_2 at –20°C.

Spectroscopic data for the title cluster: FT-IR (KBr) 3412, 2089, 2049, 2002, 1934, 1585, 1461, 568, 547 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.56 (3H, s), 2.92 (3H, d, J = 4.8), 4.24 (5H, s), 4.59 (1H, qui), 4.61 (1H, qui), 4.65(1H, qui), 4.83 (1H, s), 5.03 (1H, qui), ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.77, 32.30, 53.39, 69.30, 69.72, 69.89, 71.15, 73.26, 172.31, 172.94, 185.66, 190.43, 193.40, 197.49, 198.99, 203.72, 204.64, 204.86. Anal. *Calc*. For $C_{23}H_{16}FeN_3O_9Ru_3S$: C, 31.8; H, 1.8 Found: C, 31.7; H, 1.9%.

Crystallographic analysis of the title cluster

($C_{23}H_{16}FeN_3O_9Ru_3S$): Mr = 954.43, monoclinic, space group P2(1)/c, a = 9.2352(12), b = 22.731(3), c = 15.622(2) Å. α = 90 deg. β = 106.133(2) deg. γ = 90 deg. V = 3150.4(7) Å3, Z = 4, ρcaled = 2.012 mg m^{-3}, F(000) = 1852, crystal size 0.490 x 0.345 x 0.220 mm, R_1 = 0.0446 [wR_2 = 0.0968, I>2σ(I)]. R_1 = 0.0689 (wR_2 = 0.1026, all data), GOF = 0.858. Data/restraints/parameters of 6790/3/394,T = 293(2) K, λ = 0.71073 Å, μ = 2.15 mm^{-1}.

Data collection: Bruker SMART; cell refinement: Bruker SMART; data reduction: Bruker SHELXTL; program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: Bruker SHELXTL; software used to prepare material for publication: Bruker SHELXTL.

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