Monoclinic
$P2_1/c$
$a = 9.6467 (4)$ Å
$b = 12.7276 (6)$ Å
$c = 20.804 (1)$ Å
$\beta = 90.129 (1)°$
$V = 2554.3 (2)$ Å^3
$Z = 4$
$D_x = 1.743$ Mg m^{-3}
D_m not measured

Cell parameters from 2734
reflections
$\theta = 2.0–26.5°$
$\mu = 6.58$ mm^{-1}
$T = 203 (2)$ K
Block
$0.25 \times 0.16 \times 0.16$ mm
Red

Data collection

Bruker *P4/CCD/PC* diffrac-
tometer
φ and ω scans
Absorption correction:
empirical (*SADABS*;
Sheldrick, 1996)
$T_{min} = 0.19$, $T_{max} = 0.35$
13 422 measured reflections
5158 independent reflections

4564 reflections with
$I > 2\sigma(I)$
$R_{int} = 0.021$
$\theta_{max} = 26.5°$
$h = -12 \rightarrow 12$
$k = 0 \rightarrow 15$
$l = 0 \rightarrow 25$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.064$
$S = 1.272$
5158 reflections
316 parameters
H atoms treated by a
mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0308P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.750$ e Å^{-3}
$\Delta\rho_{min} = -0.661$ e Å^{-3}
Extinction correction: none
Scattering factors from
*International Tables for
Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

U1—N1	2.237 (3)	C1—C2	1.396 (5)
U1—Cl1	2.613 (1)	C2—C3	1.381 (6)
Cl2—C4	1.748 (4)	C3—C4	1.374 (6)
N1—HN1	0.93 (5)	C4—C5	1.371 (6)
N1—C1	1.396 (5)	C5—C6	1.386 (5)
C1—C6	1.395 (5)		
N1—U1—Cl1	93.11 (9)	C3—C2—C1	121.4 (4)
HN1—N1—C1	113 (3)	C4—C3—C2	119.7 (4)
HN1—N1—U1	103 (3)	C5—C4—C3	120.3 (4)
C1—N1—U1	143.7 (3)	C5—C4—Cl2	120.0 (3)
C6—C1—N1	122.4 (3)	C3—C4—Cl2	119.7 (3)
C6—C1—C2	117.6 (4)	C4—C5—C6	120.2 (4)
N1—C1—C2	120.0 (4)	C5—C6—C1	120.8 (4)

The pentamethylcyclopentadienyl ring defined by atoms C31–C35 was refined as two disordered pentamethylcyclopentadienyl rings. The second ring consists of atoms C31'–C35' and C31B–C35B. The site-occupancy factors of the two rings refined to 0.832 (6) for the former and 0.168 (6) for the latter. The second ring was refined with isotropic displacement parameters and no H atoms. H atoms were fixed in positions of ideal geometry, with C—H distances of 0.96 (methyl) and 0.93 Å (aromatic). The H-atom positions were refined using a riding model and the U_{iso} values were fixed to 1.2 (aromatic) or 1.5 (methyl) times the U_{eq} of the parent C atom. The amido H atom was found in the difference map and was refined with U_{iso} set to 0.08 Å^2. H atoms were not placed on the methyl groups of the disordered C5Me5 ligands.

Data collection: *SMART* (Bruker, 1996a). Cell refinement: *SAINT* (Bruker, 1996b). Data reduction: *SAINT*. Program(s)

used to solve structure: *SHELXTL* (Bruker, 1997). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

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Tetrakis(μ-6-chloropyridin-2-olato)-methoxydiruthenium(II,III)

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Abstract

The title complex, tetrakis(μ-6-chloropyridin-2-olato)-1κ^4O,2κ^4N-methoxy-1κO-diruthenium(II,III)(*Ru—Ru*), [Ru$_2$(C$_5$H$_3$ClNO)$_4$(CH$_3$O)], has a totally polar arrangement of the chp ligands (chp is 6-chloro-2-hydroxypyridine), and one methoxy group occupies the sterically available axial position. The bond distance between the

two Ru atoms is 2.2559 (5) Å. The axially coordinated methoxy group is bound to the Ru atom with an Ru—O bond distance of 2.250 (3) Å.

Comment

The 6-chloro-2-hydroxypyridine (chp) ligand is known to be a good stabilizer of a dimetal unit with short metal–metal bonds (Cotton *et al.*, 1980). In complexes of the type [M_2(chp)₄] (M = Cr, Mo, W or Rh), the disposition of the four bridging ligands about the dimetal unit is generally such that each metal is coordinated to two O atoms and two N atoms, thus giving what is called the 2:2 arrangement. In some dirhodium species, a 3:1 arrangement of ligands has been observed (Clegg *et al.*, 1982).

The first diruthenium(II,III) compound with four chp ligands was reported in 1985 as [Ru₂(chp)₄Cl], which has a totally polar arrangement of the chp ligands and an axially bonded Cl⁻ ligand (Chakravarty *et al.*, 1985). In [Ru₂(chp)₄Cl], one Ru atom is bonded to four pyridyl N atoms, while another Ru atom is coordinated by four O atoms and one Cl atom. The Ru₂⁵⁺ core has a quartet ground state based on a $\sigma^2\pi^4\delta^2(\pi^*\delta^*)^3$ electronic configuration. If the Ru₂⁵⁺ cores were coupled by bidentate ligands with a π-conjugated system, it would be possible to observe magnetic coupling phenomena between the linked Ru₂⁵⁺ cores. However, [Ru₂(chp)₄Cl] has no vacant site to which other donor ligands can bond. Therefore, a general method has been developed to introduce other ligands into the axial site instead of the Cl atom in [Ru₂(chp)₄Cl]; halide abstraction by a suitable Ag salt followed by coordination of the nitrogen-donor ligands such as pyridine or pyrazine (Cotton *et al.*, 1991) is a good example. Recently, we have proved that two [Ru₂(chp)₄]⁺ units could be connected to form pentanuclear complexes by using [Co(CN)₆]³⁻ (Kim *et al.*, 1998). In an attempt to prepare the metal cyanide-bridged pentanuclear species [Ru₂(chp)₄{Cr(CN)₆}Ru₂(chp)₄]⁻, the complex [Ru₂(chp)₄(OMe)], (I), was isolated. Its structure is reported herein.

(I)
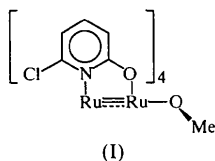
Complex (I) has four totally polarly arranged chp ligands and one axially coordinated methoxy group. The bond length between the two Ru atoms is 2.2558 (4) Å, which is very short relative to the value in [Ru₂(chp)₄Cl] [2.281 (1) Å; Chakravarty *et al.*, 1985]. The average value of the four O—Ru1—Ru2—N torsion angles of the chp ligands is about 20°, which is similar to that of

[Ru₂(chp)₄Cl] (Chakravarty *et al.*, 1985). The Ru1—O5 bond length is 2.250 (2) Å. The O4—Ru1—O5—C21 torsion angle is −0.4 (3)° and the Ru1—O5—C21 bond angle is 123.4 (3)°.
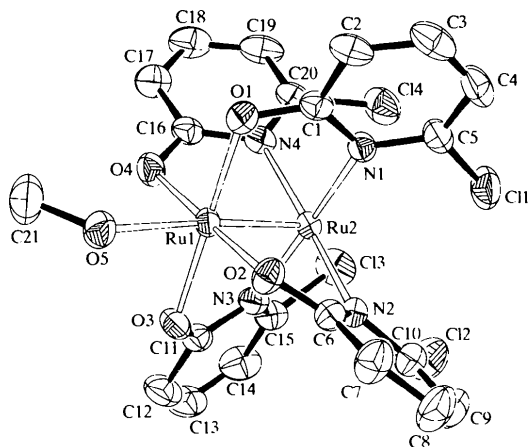

Fig. 1. *ORTEP*-3 (Farrugia, 1997) view of complex (I). Displacement ellipsoids for non-H atoms are drawn at the 50% probability level and H atoms have been omitted for clarity.

Experimental

Complex (I) was prepared by the direct diffusion technique. A solution of K₃[Cr(CN)₆] in a methanol/water mixture (1:1 *v/v*) was carefully layered with a methanol solution of [Ru₂(chp)₄]NO₃, which was obtained by the reaction of [Ru₂(chp)₄Cl] with AgNO₃. About three months later, X-ray quality dark-brown block crystals were obtained and air-dried.

Crystal data

[Ru₂(C₅H₃ClNO)₄(CH₃O)]	Mo $K\alpha$ radiation
M_r = 747.31	λ = 0.71073 Å
Triclinic	Cell parameters from 25
$P\bar{1}$	reflections
a = 9.346 (1) Å	θ = 9.13–12.50°
b = 9.516 (1) Å	μ = 1.684 mm⁻¹
c = 15.031 (1) Å	T = 293 (2) K
α = 96.62 (1)°	Block
β = 103.76 (1)°	0.35 × 0.31 × 0.29 mm
γ = 102.92 (1)°	Dark brown
V = 1245.4 (2) Å³	
Z = 2	
D_x = 1.993 Mg m⁻³	
D_m not measured	

Data collection

Enraf–Nonius CAD-4	R_{int} = 0.008
MACH-3 diffractometer	θ_{max} = 25.04°
$2\theta/\omega$ scans	h = 0 → 11
Absorption correction: none	k = −11 → 11
4672 measured reflections	l = −17 → 17
4375 independent reflections	3 standard reflections
4086 reflections with	frequency: 60 min
$I > 2\sigma(I)$	intensity decay: negligible

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.002$
$R[F^2 > 2\sigma(F^2)] = 0.028$	$\Delta\rho_{max} = 0.898$ e Å^{-3}
$wR(F^2) = 0.080$	$\Delta\rho_{min} = -1.124$ e Å^{-3}
$S = 1.132$	Extinction correction: none
4375 reflections	Scattering factors from
325 parameters	*International Tables for*
H-atom parameters	*Crystallography* (Vol. C)
constrained	
$w = 1/[\sigma^2(F_o^2) + (0.0544P)^2$	
$+ 1.1315P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. *Selected geometric parameters (Å, °)*

Ru1—O2	2.029 (2)	O5—C21	1.401 (5)
Ru1—O4	2.040 (2)	Ru2—N1	2.098 (3)
Ru1—O1	2.040 (2)	Ru2—N3	2.109 (3)
Ru1—O3	2.059 (2)	Ru2—N4	2.119 (3)
Ru1—O5	2.250 (2)	Ru2—N2	2.122 (3)
Ru1—Ru2	2.2558 (4)		
O2—Ru1—O4	178.12 (9)	O3—Ru1—Ru2	89.60 (7)
O2—Ru1—O1	87.21 (9)	O5—Ru1—Ru2	175.48 (6)
O4—Ru1—O1	91.17 (9)	C21—O5—Ru1	123.4 (3)
O2—Ru1—O3	91.72 (9)	N1—Ru2—N3	175.48 (10)
O4—Ru1—O3	89.90 (9)	N1—Ru2—N4	90.59 (10)
O1—Ru1—O3	178.93 (9)	N3—Ru2—N4	90.82 (10)
O2—Ru1—O5	86.90 (9)	N1—Ru2—N2	86.96 (10)
O4—Ru1—O5	92.23 (9)	N3—Ru2—N2	91.24 (10)
O1—Ru1—O5	93.07 (9)	N4—Ru2—N2	174.22 (10)
O3—Ru1—O5	86.80 (9)	N1—Ru2—Ru1	87.53 (7)
O2—Ru1—Ru2	90.47 (6)	N3—Ru2—Ru1	88.24 (7)
O4—Ru1—Ru2	90.51 (6)	N4—Ru2—Ru1	87.23 (7)
O1—Ru1—Ru2	90.47 (6)	N2—Ru2—Ru1	87.43 (7)
O4—Ru1—O5—C21	−0.4 (3)	O4—Ru1—Ru2—N4	20.60 (10)
O1—Ru1—Ru2—N1	20.13 (10)	O2—Ru1—Ru2—N2	19.98 (10)
O3—Ru1—Ru2—N3	19.59 (10)		

Except for some residual electron density in the region of Ru2 (deepest hole -1.12 e Å^{-3} at 1.03 Å from Ru2), the final difference map showed no significant features.

Data collection: *CAD-4-PC Software* (Enraf–Nonius, 1992). Cell refinement: *CAD-4-PC Software*. Data reduction: *XCAD4* (Harms, 1997). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997b). Molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997). Software used to prepare material for publication: *SHELXL97*.

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