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Regioisomerism displayed by the 6-chloro-2-oxopyridinate complexes of Ru_2^{4+} and Ru_2^{5+}

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Abstract

Three new compounds containing either the Ru_2^{4+} or the Ru_2^{5+} core surrounded by four chp^- ligands (where chp^- represents the anion of 2-hydroxy-6-chloropyridine) have been prepared and structurally characterized. 2,2-*Trans*-$[Ru_2(chp)_4]$ (**1**) was obtained by reaction of $Ru_2(O_2CCH_3)_4Cl$ with molten Hchp (via the unisolated intermediate 0,4-$[Ru_2(chp)_4Cl]$). It crystallizes in space group *Pbca* (No. 61) with $a = 16.073(5)$, $b = 18.603(5)$, $c = 15.594(2)$ Å, $V = 4663(2)$ Å^3, $Z = 8$. The Ru–Ru distance is 2.248(1) Å. 0,4-$[Ru_2(chp)_4(THF)]\cdot THF$ (**2**) was obtained by reduction of 0,4-$[Ru_2(chp)_4Cl]$ with zinc. It forms monoclinic crystals in space group $P2_1/c$ (No. 14) with $a = 13.616(2)$, $b = 12.820(3)$, $c = 18.673(2)$ Å, $\beta = 97.39(4)°$, $V = 3233(1)$ Å^3, $Z = 4$. The Ru–Ru distance is 2.261(1) Å. The compound $\{0,4\text{-}[Ru_2(chp)_4]\}_2(BF_4)_2$ (**3**) was obtained from 0,4-$[Ru_2(chp)_4Cl]$ by removal of Cl^- with $Ag(CH_3CN)_4BF_4$. It crystallizes in space group $P\bar{1}$ (No. 2) with $a = 12.995(3)$, $b = 13.459(3)$, $c = 10.640(3)$ Å, $\alpha = 106.54(2)$, $\beta = 93.48(2)$, $\gamma = 65.78(2)°$, $V = 1623.5(7)$ Å^3, $Z = 1$. The Ru–Ru distance is 2.254(1) Å.

Keywords: Crystal structures; Regioisomerism; Ruthenium complexes; 6-Chloro-2-oxopyridinate complexes

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1. Introduction

It is well known that for compounds containing M_2^{n+} units bridged by four ligands of the general type **1**, and when X and Z are different, four ligand arrangements are possible. They are shown schematically as **2–5**, and all have been observed [1]. One specific type of ligand that has given rise to a large number of such compounds is the 2-oxopyridinate anion, **6**, which is normally encountered in one of the five varieties shown as **6a–6e**.

While the term has not previously been employed with respect to compounds of this type, we believe that it would be useful, and not inconsistent with usage established in organic chemistry, to refer to **2**, **3** and **4/5** as regioisomers. Structures **4** and **5** would then be described as geometric isomers of the 2,2 regioisomer. They have been called *trans* and *cis* or *transoid* and *cisoid* isomers in previous literature and have also been designated by their point group symmetries, D_{2d} and C_{2h}, respectively. There are no general criteria for predicting which of the arrangements, **2–5**, will be preferred, although in a few specific cases the observation can be rationalized.

This report is concerned with cases of regioisomerism manifested in the chemistries of the Ru_2^{4+} and Ru_2^{5+} units. Our knowledge of the chemical and structural properties of complexes of the dinuclear units Ru_2^{4+}, Ru_2^{5+} and Ru_2^{6+} has increased enormously in the past decade [1,2]. For the $Ru_2(O_2CR)_4$ and $[Ru_2(O_2CR)_4]^+$ species, where much of the effort has been centered, it has been shown that the electronic structures, insofar as Ru–Ru bonding is concerned, are $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*2}$ and $\sigma^2\pi^4\delta^2\delta^{*}\pi^{*2}$, respectively. Since these differ by only one δ^* electron, their Ru–Ru distances are expected to be very similar, and, in fact, they are. However, the comparisons are clouded because there is no pair of compounds so far reported in which there is not some difference in the number and/or nature of the axial ligands. Axial ligands must have some effect on the Ru–Ru distance in each case, and therefore it is not possible to get an unambiguous picture of how the loss of one δ^* electron, in and of itself, affects the Ru–Ru bond [1].

We have previously reported that the compound '$Ru_2(chp)_4$' exists as a dimer of this formula, as shown in Fig. 1 [3]. It can be seen that each of the two identical subunits of this dimer is the 1,3 regioisomer, that is, three of the chp ligands are oriented so as to place their 6-chloro subunits around the *exo* axial positions. This makes the *exo* positions too sterically encumbered to accept an axial ligand.

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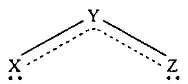

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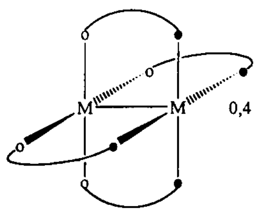

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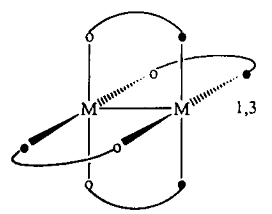

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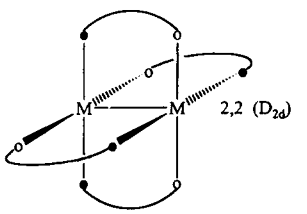

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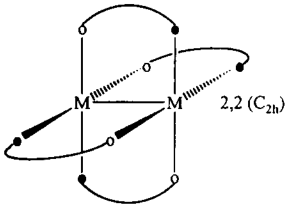

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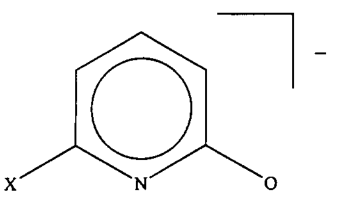


6

6a X = H	hp
6b X = CH_3	mhp
6c X = F	fhp
6d X = Cl	chp
6e X = Br	bhp

The dimerization occurs through the sharing of one oxygen atom coordinated to the *endo* metal atom of one subunit with the *endo* metal atom of another.

The work reported here extends the previous study [3] of $[Ru_2(chp)_4]_2$ in two respects. First, it has been found that this compound can also be obtained in the un-dimerized form, namely the 2,2 isomer, analogous to its $Ru_2(mhp)_4$ and $Ru_2(bhp)_4$ homologues [3]. In addition, by employing still another preparative route, we have obtained 0,4-$[Ru_2(chp)_4(THF)]$. This is not the first example of an $M_2(xhp)_4$ compound existing as both the 2,2 (D_{2d}) molecule and the dimer of the 1,3 regioisomer. The analogous situation was found some time ago for the $Rh_2(mhp)_4$ and $[Rh_2(mhp)_4]_2$ molecules [4,5]. It is, however, the first example of three regioisomeric compounds.

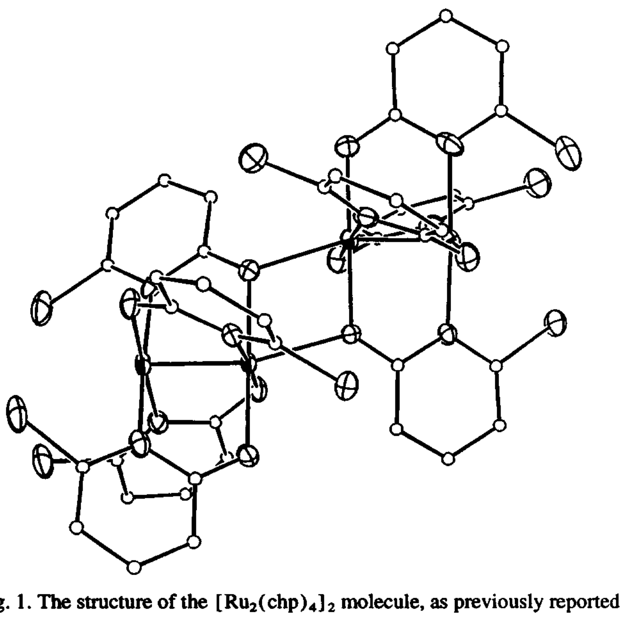


Fig. 1. The structure of the $[Ru_2(chp)_4]_2$ molecule, as previously reported [3].

The second part of the work reported here was carried out in the hope that the arrangement found in $[Ru_2(chp)_4]_2$ might prevail in the $[Ru_2(chp)_4]^+$ ion, thereby affording the opportunity to compare two species that differ only electronically and not compositionally, namely $[Ru_2(chp)_4]_2$ and $[Ru_2(chp)_4]_2^{2+}$. We have, accordingly, prepared and characterized the latter in the compound having BF_4^- as the counterion. It is found, however, that the dinuclear subunits in the cation are the 0,4 regioisomer.

2. Experimental

The starting materials employed in the syntheses, $Ru_2(O_2CCH_3)_4Cl$ [6] and 0,4-$[Ru_2(chp)_4Cl]$ [7], were prepared by previously described procedures. All reactions were performed under dry N_2 in standard Schlenkware. 6-Chloro-2-pyridinol was purchased from Pfalz and Bauer Chemical Co., and purified by recrystallization followed by sublimation. Zn powder was purchased from Aldrich Chemical Co. and used as received. $Ag(CH_3CN)_4BF_4$ was prepared by recrystallization of $AgBF_4$ from freshly distilled CH_3CN. All solvents were of reagent grade or better, from commercial sources, and freshly distilled under N_2 in the presence of a suitable drying agent.

2.1. Preparation of 2,2-$[Ru_2(chp)_4]$ (1)

In a Schlenk tube, 0.5 g (1 mmol) $Ru_2(O_2CCH_3)_4Cl$ and 5.0 g (39 mmol) Hchp were mixed. After careful exclusion of all air by repeated evacuation and refilling with dry N_2, the mixture was heated in an oil bath to a temperature in excess of 150 °C for several hours. As the Hchp melted the initial color of the resulting liquid was the purple color characteristic of $Ru_2(chp)_4Cl$. However, upon further heating, the mixture changed color to a deep brown. Excess Hchp remaining was removed by sublimation, leaving behind a dark residue. The residue was extracted with several portions of CH_2Cl_2, which took on a dark orange–brown color. The solutions were collected together, filtered, concentrated by evaporation, and hexanes carefully layered on top. During the course of several days, upon diffusion of the hexanes into the dichloromethane solution, large block-shaped crystals grew. Yield 0.67 g (89%). The compound is extremely air stable, and a solution of this compound in toluene exposed to air for several days did not show any color change.

2.2. Preparation of 0,4-$Ru_2(chp)_4(THF)\cdot THF$ (2)

In a Schlenk tube were placed 0.15 g (0.18 mmol) $Ru_2(chp)_4Cl\cdot CH_2Cl_2$ and 0.022 g (0.34 mmol) Zn powder.

After careful exclusion of all air by repeated evacuation and refilling with dry N_2, 20 ml of freshly distilled THF were added through a rubber septum. Stirring of the resulting solution for a few hours resulted in a color change from the purple color associated with $Ru_2(chp)_4Cl$ to yellow–orange. The solution was then filtered, and freshly distilled hexanes carefully layered on top of this solution, and the tube placed in a refrigerator kept at −20 °C. During the course of several days, upon diffusion of the hexanes into the THF solution large block-shaped crystals grew. Yield 0.14 g (93%). This compound is extremely air sensitive, and exposure of a THF solution to air results in an immediate color change to the characteristic purple color of $Ru_2(chp)_4{}^+$.

2.3. *Preparation of 0,4-[$Ru_2(chp)_4$]$_2$(BF_4)$_2$ (3)*

In a round bottom flask fitted with a condenser were placed 0.17 g (0.20 mmol) $Ru_2(chp)_4Cl \cdot CH_2Cl_2$ and 0.072 g (0.20 mmol) $Ag(CH_3CN)_4BF_4$ [8]. After careful exclusion of all air by repeated evacuation and refilling with dry N_2, 20 ml of freshly distilled CH_2Cl_2 were added under a flow of dry N_2. The resulting solution was refluxed for 5 h. After it had cooled and the AgCl had been removed by filtration, the purple solution was layered with hexanes. Over the course of a few days block shaped crystals were obtained in about 80% yield.

2.4. *X-ray crystallography*

2.4.1. *Compound 1*

A single crystal of dimensions 0.4×0.3×0.3 mm was embedded in epoxy glue, mounted on a glass fiber and placed on a Nicolet P3/F automated diffractometer. The cell constants and crystal orientation parameters were determined from a list of twenty-five reflections found by an automated search routine. The Laue symmetry of *mmm* was confirmed through axial photographs. Pertinent information on data col-

Table 1
Crystal data and structure refinement details

Compound	2,2-*trans*-$Ru_2(chp)_4$ (**1**)	4,0-$Ru_2(chp)_4(THF) \cdot (THF)$ (**2**)	{0,4-[$Ru_2(chp)_4$]}$_2$(BF_4)$_2 \cdot$4(CH_2Cl_2) (**3**)
Empirical formula	$C_{20}H_{12}Cl_4N_4O_4Ru_2$	$C_{28}H_{28}Cl_4N_4O_6Ru_2$	$Ru_4Cl_{16}O_8N_8C_{44}B_2F_8H_{32}$
Formula weight	716.29	860.51	1945.92
Space group	*Pbca*	$P2_1/c$	$P\bar{1}$
Unit cell dimensions			
a (Å)	16.073(5)	13.616(2)	12.995(3)
b (Å)	18.603(5)	12.820(3)	13.459(3)
c (Å)	15.594(2)	18.673(2)	10.640(3)
α (°)			106.54(2)
β (°)		97.39(4)	93.48(2)
γ (°)			65.78(2)
Volume (Å^3)	4663(2)	3232.6(9)	1623.5(7)
Z	8	4	1
Density (calc.) (g cm^{-3})	2.040	1.7682	1.9903
Crystal size (mm)	0.4×0.3×0.3	0.3×0.3×0.3	0.15×0.20×0.25
Absorption coefficient (mm^{-1})	1.770	1.2963	1.6372
Data collection instrument	Nicolet P3/F	Enraf-Nonius CAD4-FAST	Nicolet P3/F
Wavelength (Å)	0.71073	0.71073	0.71073
Orientation reflections: no., range (2*θ*)	25, 20–30	250, 20.5–41.6	25, 20–29
Temperature (K)	293(2)	213(2)	293(2)
Scan method	*θ*–2*θ*	*ω*	*θ*–2*θ*
θ Range for data collection (°)	2.12–22.54	2.20–22.50	2.0–22.50
Reflections collected	1708	9836	4468
Independent reflections	1708	3688 (R(int) = 0.0718)	4468
Data/restraints/parameters	1705/0/320	3677/78/428	3489/0/401
Software used for structure refinement	SHELXL-93	SHELXL-93	VAX-SDP
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F
Final *R* indices ($I > 2\sigma(I)$)	$R1$ [a] = 0.037, $wR2$ [b] = 0.090	$R1$ [a] = 0.044, $wR2$ [b] = 0.107	R [a] = 0.066, Rw [c] = 0.083 ($I > 3\sigma(I)$)
R indices (all data)	$R1$ [a] = 0.042, $wR2$ [b] = 0.094	$R1$ [a] = 0.051, $wR2$ [b] = 0.124	
Goodness-of-fit (*GOF*)	1.050 [d]	1.123 [d]	1.683 [e]
Largest shift/e.s.d., final cycle	0.000	−0.003	0.03
Largest peak, final cycle (e Å^{-3})	1.43(12)	0.89(13)	1.894

[a] R or $R1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$.

[b] $wR2 = \{\Sigma[w(F_o{}^2 - F_c{}^2)^2] / \Sigma[w(F_o{}^2)^2]\}^{1/2}$.

[c] $Rw = \{\Sigma[w(|F_o| - |F_c|)^2] / \Sigma[w|F_o|^2]\}^{1/2}$.

[d] $GOF = \{\Sigma[w(F_o{}^2 - F_c{}^2)^2] / (n_{obs} - n_{para})\}^{1/2}$.

[e] $GOF = \{\Sigma[w(|F_o| - |F_c|)^2] / (n_{obs} - n_{para})\}^{1/2}$.

For SHELXL-93 $w = 1/[\sigma^2(F_o{}^2) + (a^*P)^2\} + b^*P]$, $P = (F_o{}^2 + 2F_c{}^2)/3$.

For VAX-SDP $w = 1/\sigma^2(|F_o|)$.

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **1**

	x	y	z	U_{eq} [a]
Ru(1)	1652(1)	746(1)	1261(1)	30(1)
Ru(2)	2052(1)	1903(1)	1233(1)	33(1)
Cl(1)	1506(2)	−621(2)	2416(2)	66(1)
O(1)	2173(5)	1930(4)	2543(4)	41(2)
N(1)	1871(5)	726(4)	2575(5)	35(2)
C(11)	2080(7)	1352(6)	2983(6)	34(3)
C(12)	2210(6)	1324(6)	3886(6)	33(3)
C(13)	2124(7)	688(7)	4301(7)	46(3)
C(14)	1920(7)	64(7)	3890(7)	45(3)
C(15)	1794(7)	118(6)	3030(7)	36(3)
Cl(2)	3609(2)	2910(2)	1146(3)	76(1)
O(2)	2839(4)	396(4)	1041(4)	39(2)
N(2)	3281(6)	1562(5)	1109(5)	36(2)
C(21)	3450(7)	835(6)	1056(6)	37(3)
C(22)	4284(9)	627(8)	986(8)	61(4)
C(23)	4890(9)	1108(9)	987(9)	78(5)
C(24)	4729(9)	1838(8)	1029(8)	70(5)
C(25)	3912(8)	2015(6)	1091(7)	45(3)
Cl(3)	926(2)	−489(1)	143(2)	45(1)
O(3)	1957(5)	1957(4)	−74(4)	42(2)
N(3)	1448(5)	824(4)	−60(5)	34(2)
C(31)	1632(7)	1427(5)	−495(7)	37(3)
C(32)	1479(8)	1469(7)	−1380(7)	49(3)
C(33)	1124(8)	896(6)	−1773(8)	58(4)
C(34)	937(7)	261(7)	−1338(7)	52(3)
C(35)	1122(6)	255(6)	−479(7)	36(3)
Cl(4)	1366(2)	3478(2)	1077(2)	68(1)
O(4)	443(4)	1019(4)	1516(4)	42(2)
N(4)	803(6)	2192(4)	1336(5)	36(2)
C(41)	212(8)	1683(6)	1473(6)	40(3)
C(42)	−638(8)	1881(8)	1559(8)	60(4)
C(43)	−816(10)	2596(8)	1492(9)	72(5)
C(44)	−244(10)	3097(8)	1343(8)	65(4)
C(45)	557(9)	2888(6)	1255(8)	50(3)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

lection and reduction is given in Table 1. The space group was determined to be *Pbca* (No. 61) from systematic absences prior to solution. The positions of the metal atoms and the first coordination sphere were determined by direct methods as programmed in SHELXS-86 [10]. The remaining non-hydrogen atoms were found through successive cycles of alternating least-squares refinements followed by Fourier maps. Hydrogen atoms were placed in idealized positions and their isotropic temperature factors tied to one free variable. The length of each C–H bond was then allowed to refine to an equilibrium position without changing direction. All non-hydrogen atoms were refined anisotropically. Positional parameters, isotropic displacement parameters and their e.s.d.s can be found in Table 2.

2.4.2. *Compound* 2

A very well shaped single crystal of dimensions 0.3 × 0.3 × 0.3 mm was mounted on a quartz fiber with a dab of silicone grease and quickly placed on the cold stream, at −60 °C, of an Enraf-Nonius CAD4-FAST automated diffractometer equipped with a low temperature device. The cell constants and crystal orientation parameters were determined from a list of twenty-five reflections found by an automated search routine, which were refined against a list of 250 reflections also found through the use of an automated search routine. The Laue symmetry of $2/m$ was confirmed through axial images. Pertinent information on data collection and reduction are given in Table 1. The space group was determined to be $P2_1/c$ (No. 14) from systematic absences prior to solution. The positions of the metal atoms and the first coordination sphere were determined by direct methods as

Table 3
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **2**

	x	y	z	U_{eq} [a]
Ru(1)	7893(1)	1991(1)	156(1)	21(1)
Ru(2)	7085(1)	3518(1)	240(1)	24(1)
Cl(1)	8577(1)	575(1)	−1199(1)	34(1)
O(1)	6096(3)	3134(4)	−633(2)	32(1)
N(1)	7193(3)	1888(4)	−928(2)	22(1)
C(11)	6365(4)	2493(5)	−1115(3)	27(1)
C(12)	5829(5)	2402(6)	−1805(3)	35(2)
C(13)	6139(5)	1743(6)	−2308(4)	40(2)
C(14)	6998(5)	1156(6)	−2125(3)	34(2)
C(15)	7490(4)	1261(5)	−1444(3)	28(1)
Cl(2)	7220(1)	−503(1)	−20(1)	38(1)
N(2)	6670(3)	1234(4)	529(2)	26(1)
O(2)	6188(3)	2849(4)	916(2)	30(1)
C(21)	6049(4)	1857(5)	888(3)	27(1)
C(22)	5278(5)	1386(5)	1213(3)	31(2)
C(23)	5127(5)	336(6)	1169(3)	38(2)
C(24)	5728(5)	−288(6)	788(3)	37(2)
C(25)	6457(4)	200(5)	487(3)	29(2)
Cl(3)	8890(1)	205(1)	1361(1)	41(1)
O(3)	8082(3)	3941(3)	1112(2)	29(1)
N(3)	8560(3)	2210(4)	1229(2)	25(1)
C(31)	8588(5)	3218(6)	1490(3)	31(2)
C(32)	9158(5)	3474(6)	2149(3)	39(2)
C(33)	9625(6)	2690(7)	2566(4)	53(2)
C(34)	9540(6)	1656(7)	2344(4)	49(2)
C(35)	9014(5)	1477(5)	1680(3)	31(2)
Cl(4)	10277(1)	1324(1)	192(1)	38(1)
N(4)	9060(3)	2863(4)	−205(2)	22(1)
O(4)	7956(3)	4224(3)	−430(2)	33(1)
C(41)	8831(4)	3842(5)	−474(3)	26(1)
C(42)	9553(5)	4438(6)	−785(3)	37(2)
C(43)	10484(5)	4046(6)	−781(3)	37(2)
C(44)	10731(5)	3070(6)	−485(3)	37(2)
C(45)	9996(4)	2530(5)	−207(3)	28(1)
O(5)	6242(4)	5012(3)	334(2)	41(1)
C(51)	6162(7)	5498(6)	1024(4)	59(3)
C(52)	6567(7)	6558(7)	971(5)	78(4)
C(53)	6293(7)	6831(7)	208(6)	85(4)
C(54)	6249(7)	5844(6)	−191(4)	66(3)
O(61)	3433(50)	2393(10)	−2650(50)	106(30)
O(62)	3574(7)	2339(10)	−2902(10)	119(7)
C(61)	3374(9)	1276(10)	−2733(8)	129(6)
C(62)	2318(8)	1132(10)	−2973(8)	147(8)
C(63)	1959(10)	2039(10)	−3408(8)	127(6)
C(64)	2655(9)	2866(10)	−3141(8)	124(5)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4
Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for **3**

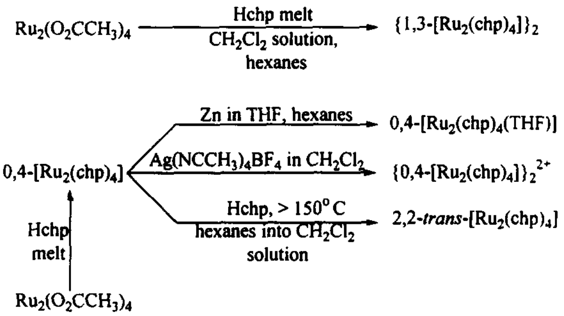
	x	y	z	U_{eq} [a]
Ru(1)	3834.7(7)	810.2(7)	993.1(9)	21.5(2)
Ru(2)	2444.6(7)	2537.5(7)	1132.1(9)	21.1(2)
Cl(1)	2307(3)	4984(2)	−891(4)	44(9)
O(1)	5382(5)	−893(5)	524(7)	23(2)
N(1)	3549(7)	2799(7)	3(9)	24(2)
C(11)	4443(8)	1890(8)	−690(10)	24(2)
C(12)	5134(9)	1991(9)	−1550(10)	32(3)
C(13)	4940(10)	3040(10)	−1660(10)	42(3)
C(14)	4050(10)	4017(9)	−910(10)	42(3)
C(15)	3410(10)	3829(9)	−100(10)	31(3)
Cl(2)	−761(3)	6252(3)	978(4)	41.8(8)
N(2)	1882(6)	1752(7)	−597(9)	23(2)
O(2)	3017(6)	53(6)	−248(7)	27(2)
C(21)	2266(8)	601(9)	−960(10)	25(2)
C(22)	1880(10)	10(10)	−2060(10)	36(3)
C(23)	1130(10)	600(10)	−2790(10)	46(4)
C(24)	710(10)	1810(10)	−2450(10)	37(4)
C(25)	1136(9)	2305(9)	−1390(10)	30(3)
Cl(3)	−355(3)	3747(3)	1770(4)	46.8(9)
O(3)	3113(6)	666(6)	2456(8)	31(2)
N(3)	1466(7)	2134(7)	2248(9)	26(2)
C(31)	2029(9)	1234(9)	2740(10)	28(3)
C(32)	1470(10)	910(10)	3540(10)	38(3)
C(33)	320(10)	1520(10)	3800(10)	39(3)
C(34)	−260(10)	2430(10)	3260(10)	38(3)
C(35)	328(9)	2679(9)	2510(10)	32(3)
Cl(4)	1231(3)	4946(3)	3614(4)	49(1)
N(4)	3148(8)	3174(7)	2838(9)	28(2)
O(4)	4722(6)	1495(6)	2212(8)	28(2)
C(41)	4272(9)	2521(9)	2970(10)	30(3)
C(42)	4880(10)	2930(10)	3940(10)	44(4)
C(43)	4360(10)	4010(10)	4820(10)	48(4)
C(44)	3910(10)	4680(10)	4690(10)	44(3)
C(45)	2690(10)	4220(10)	3750(10)	37(3)
B	2400(20)	7800(20)	4150(20)	55(5)
F(1)	2447(8)	7599(8)	5333(9)	71(3)
F(2)	3127(8)	8288(8)	4040(10)	92(3)
F(3)	1369(9)	8610(10)	4100(10)	13.6(4)
F(4)	2740(20)	6890(20)	3220(20)	16.9(7) *
C(71)	3790(20)	1510(10)	5460(20)	73(5)
Cl(71)	6220(4)	−588(4)	3732(5)	84(1)
Cl(72)	2553(6)	2832(5)	−3950(6)	104(2)
C(81)	2260(20)	−2130(20)	430(20)	110(10)
Cl(81)	3049(6)	−2921(5)	−1151(8)	108(2)
Cl(82)	974(5)	−1178(6)	193(7)	114(2)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. Starred atoms were refined isotropically.

programmed in SHELXS-86. The remaining non-hydrogen atoms were found through successive cycles of alternating least-squares refinements followed by Fourier maps. Hydrogen atoms were placed in idealized positions and their isotropic temperature factors tied to one free variable. The C–H bond length was then allowed to refine to an equilibrium position. All non-hydrogen atoms were refined anisotropically. The unit cell also contains THF of crystallization which displayed disorder in the position of the oxygen atom over two sites, as is frequently the case. The site occupation factor for each of the sites was modeled in such a way that the sum was required to be unity. Positional parameters, isotropic displacement parameters and their e.s.d.s can be found in Table 3.

2.4.3. Compound 3

A block-shaped crystal (0.15 × 0.2 × 0.25 mm) was mounted on a glass fiber with epoxy resin. The data were collected on a Nicolet P3/F diffractometer equipped with Mo Kα radiation. The determination of the crystal system, data collection procedure, structure solution, and refinement were all carried out by routine procedures. The approximate positions of the ruthenium atoms were derived from a Patterson map, and the other non-hydrogen atoms were found in an alternating series of difference Fourier maps and least-squares refinements in the VAX-SDP package. All but one F atom were refined with anisotropic thermal parameters. The BF_4^- ions showed considerable thermal motion, as is often the case, but did not appear to be actually disordered. The



Scheme 1.

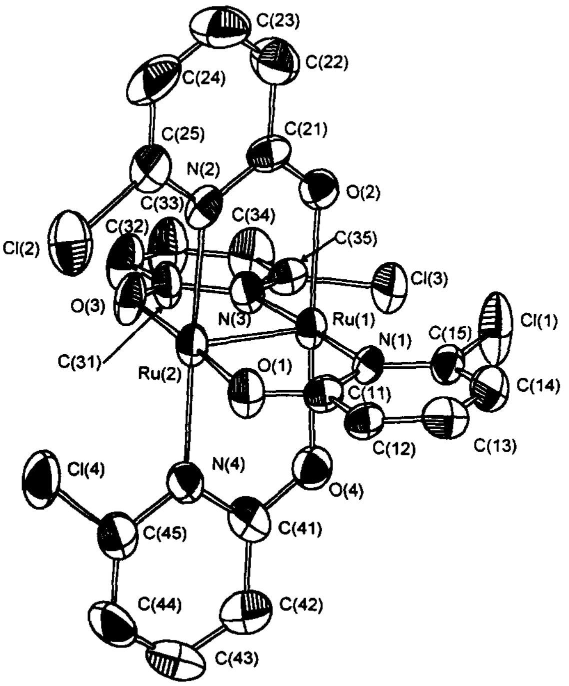


Fig. 2. The structure of 2,2-*trans*-[$Ru_2(chp)_4$]. Atoms are represented by thermal displacement ellipsoids drawn at the 40% probability level.

crystallographic data are summarized in Table 1, and the final positional parameters are listed in Table 4.

3. Results and discussion

3.1. Chemical procedures

The chemical procedures employed to obtain the four compounds under discussion are summarized in Scheme 1. The courses of some of the reactions are straightforward and obvious, while for others, this is not the case. Thus, the conversion of 0,4-[$Ru_2(chp)_4Cl$] to the {0,4-[$Ru_2(chp)_4$]}$_2^{2+}$ cation under mild conditions is reasonable and expected, as is also the conversion of the same starting material by zinc reduction to 0,4-[$Ru_2(chp)_4(THF)$]. The previously reported conversion of $Ru_2(O_2CCH_3)_4$ to the tetranuclear product containing two 1,3-[$Ru_2(chp)_4$] subunits, rather than a simple dinuclear 2,2 regioisomer, however, remains surprising.

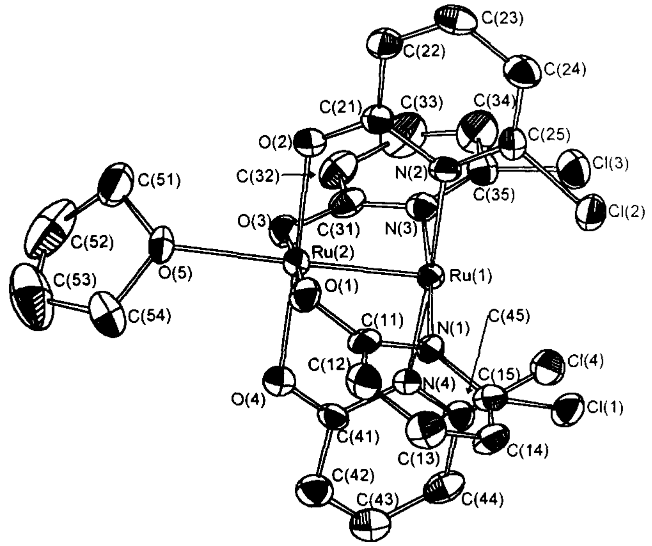


Fig. 3. The structure of 0,4-[$Ru_2(chp)_4(THF)$]. Atoms are represented as in Fig. 2.

The conversion of the 0,4-[$Ru_2(chp)_4Cl$] starting material to 2,2-*trans*-[$Ru_2(chp)_4$] is the most surprising reaction of all. First the efficient reduction of the Ru_2^{5+} core to Ru_2^{4+} was not anticipated. The only possible reducing agent is Hchp, but we do not know what this is oxidized to. It should be noted that the conversion of $Ru_2(O_2CCH_3)_4Cl$ (presumably via $Ru_2(mhp)_4Cl$) to $Ru_2(mhp)_4$ was reported several years ago [9], but the yield was only 8% rather than the high (89%) yield obtained here. Second, there is a realignment of the ligands from 0,4 to 2,2 and it is not known how this occurs.

3.2. Structures

Turning now to the structural results, the three new structures are depicted in Figs. 2, 3 and 4, and the important molecular dimensions are listed in Tables 5, 6 and 7.

For the three Ru_2^{4+} compounds, the previously reported dimer of the 1,3-isomer, as well as **1** and **2**, we have the following Ru–Ru distances and mean torsion angles, taking the compounds in the above order: 2.247(1) Å, 20.4°; 2.248(1) Å, 5.2°; 2.261(1) Å, 18.8°. The variation in Ru–Ru bond lengths is insignificant, and all of them are in the range expected [1] for Ru_2^{4+} species. Since all of these compounds should have the $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*2}$ electron configuration, there is no net δ bond to oppose internal torsion away

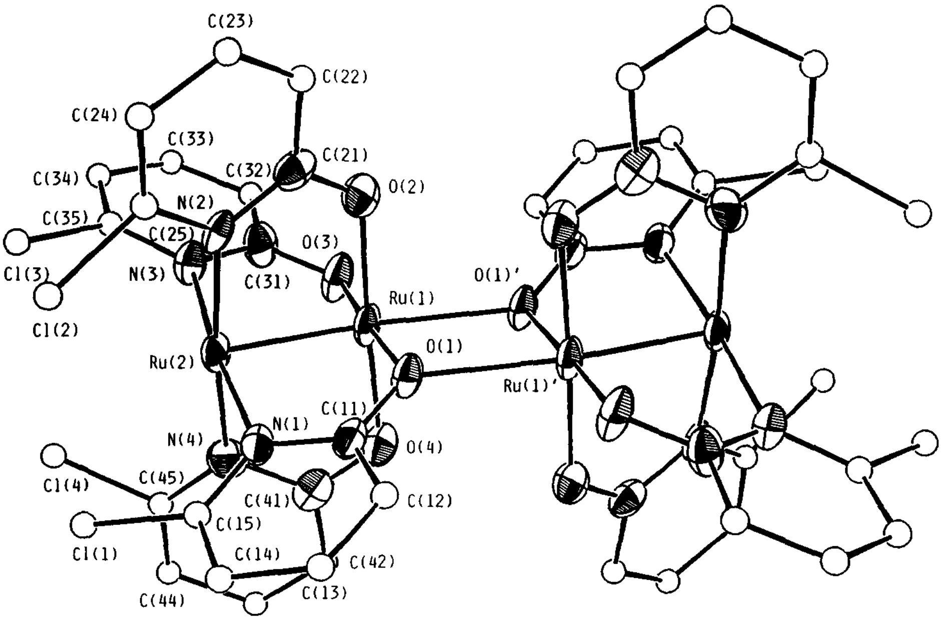


Fig. 4. The structure of the [$Ru_2(chp)_4$]$_2^{2+}$ ion as determined in the present work. Carbon and chlorine atoms are represented by circles of arbitrary size while all other atoms are represented by thermal displacement ellipsoids drawn at the 50% probability level.

Table 5
Selected bond lengths (Å) and angles (°) for **1**

Ru(1)–O(2)	2.045(7)	Ru(1)–O(4)	2.048(7)
Ru(1)–N(1)	2.081(8)	Ru(1)–N(3)	2.091(8)
Ru(1)–Ru(2)	2.248(1)	Ru(2)–O(3)	2.046(7)
Ru(2)–O(1)	2.052(7)	Ru(2)–N(2)	2.083(9)
Ru(2)–N(4)	2.084(9)		
O(2)–Ru(1)–O(4)	175.6(3)	O(2)–Ru(1)–N(1)	90.1(3)
O(4)–Ru(1)–N(1)	88.5(3)	O(2)–Ru(1)–N(3)	90.2(3)
O(4)–Ru(1)–N(3)	91.4(3)	N(1)–Ru(1)–N(3)	176.9(3)
O(2)–Ru(1)–Ru(2)	92.0(2)	O(4)–Ru(1)–Ru(2)	92.1(2)
N(1)–Ru(1)–Ru(2)	89.3(2)	N(3)–Ru(1)–Ru(2)	87.7(2)
O(3)–Ru(2)–O(1)	175.6(3)	O(3)–Ru(2)–N(2)	89.6(3)
O(1)–Ru(2)–N(2)	90.5(3)	O(3)–Ru(2)–N(4)	89.6(3)
O(1)–Ru(2)–N(4)	90.5(3)	N(2)–Ru(2)–N(4)	177.0(3)
O(3)–Ru(2)–Ru(1)	92.6(2)	O(1)–Ru(2)–Ru(1)	91.8(2)
N(2)–Ru(2)–Ru(1)	88.9(2)	N(4)–Ru(2)–Ru(1)	88.3(2)

Symmetry transformations used to generate equivalent atoms.

Table 6
Selected bond lengths (Å) and angles (°) for **2**

Ru(1)–N(3)	2.109(5)	Ru(1)–N(2)	2.121(5)
Ru(1)–N(4)	2.123(5)	Ru(1)–N(1)	2.129(4)
Ru(1)–Ru(2)	2.2609(8)	Ru(2)–O(1)	2.036(4)
Ru(2)–O(4)	2.042(4)	Ru(2)–O(2)	2.055(4)
Ru(2)–O(3)	2.055(4)	Ru(2)–O(5)	2.251(4)
N(3)–Ru(1)–N(2)	90.6(2)	N(3)–Ru(1)–N(4)	89.0(2)
N(2)–Ru(1)–N(4)	175.4(2)	N(3)–Ru(1)–N(1)	175.8(2)
N(2)–Ru(1)–N(1)	90.5(2)	N(4)–Ru(1)–N(1)	89.6(2)
N(3)–Ru(1)–Ru(2)	88.5(1)	N(2)–Ru(1)–Ru(2)	87.9(1)
N(4)–Ru(1)–Ru(2)	87.5(1)	N(1)–Ru(1)–Ru(2)	87.5(1)
O(1)–Ru(2)–O(4)	89.7(2)	O(1)–Ru(2)–O(2)	90.4(2)
O(4)–Ru(2)–O(2)	178.3(2)	O(1)–Ru(2)–O(3)	178.7(2)
O(4)–Ru(2)–O(3)	89.5(2)	O(2)–Ru(2)–O(3)	90.4(2)
O(1)–Ru(2)–O(5)	88.7(2)	O(4)–Ru(2)–O(5)	90.8(2)
O(2)–Ru(2)–O(5)	87.5(2)	O(3)–Ru(2)–O(5)	90.3(2)
O(1)–Ru(2)–Ru(1)	90.7(1)	O(4)–Ru(2)–Ru(1)	90.9(1)
O(2)–Ru(2)–Ru(1)	90.8(1)	O(3)–Ru(2)–Ru(1)	90.3(1)
O(5)–Ru(2)–Ru(1)	178.2(1)		

Symmetry transformations used to generate equivalent atoms.

from the fully eclipsed structure. Accordingly, in the 1,3 and 0,4 regioisomers, where substantial Cl to Cl non-bonded contacts can be mitigated by twisting, relatively large torsion angles of 19–20° are found. For the 2,2 compound where the driving force is less, with only two Cl atoms at each end, the torsion is less, viz. about 5°. The fact that the Ru--Ru distance in **3** is not significantly different from those in the Ru_2^{4+} compounds is consistent with (and virtually demands) the belief that the electron lost in going to this Ru_2^{5+} species is a δ^* and not a π^* electron, since the loss of a π^* electron would be expected to cause a shortening of 0.04–0.07 Å.

In the structures of $\{1,3\text{-}[Ru_2(chp)_4]\}_2$ and the cation of compound **3**, the axial linkages connecting the component dinuclear moieties are essentially the same. The mean Ru–N distances are also practically the same, but the equatorial Ru–O bonds are 0.07–0.08 Å shorter in the cation as might be expected when the effective nuclear charge on the metal atom is increased in an appreciably ionic Ru–O bond.

Table 7
Selected bond lengths (Å) and angles (°) for **3**

Ru(2)–N(3)	2.11(1)	Ru(2)–N(2)	2.098(9)
Ru(2)–N(4)	2.103(9)	Ru(2)–N(1)	2.12(1)
Ru(1)–Ru(2)	2.254(1)	Ru(1)–O(1)	2.013(8)
Ru(1)–O(4)	1.968(8)	Ru(1)–O(2)	1.966(8)
Ru(1)–O(3)	1.959(9)	Ru(1)–O(1)′	2.289(5)
N(3)–Ru(2)–N(2)	89.8(4)	N(3)–Ru(2)–N(4)	90.8(4)
N(2)–Ru(2)–N(4)	174.4(3)	N(3)–Ru(2)–N(1)	174.8(3)
N(2)–Ru(2)–N(1)	90.1(4)	N(4)–Ru(2)–N(1)	88.8(4)
N(3)–Ru(2)–Ru(1)	87.3(2)	N(2)–Ru(2)–Ru(1)	86.9(2)
N(4)–Ru(2)–Ru(1)	87.6(2)	N(1)–Ru(2)–Ru(1)	87.5(2)
O(1)–Ru(1)–O(4)	89.5(3)	O(1)–Ru(1)–O(2)	89.8(3)
O(4)–Ru(1)–O(2)	177.1(2)	O(1)–Ru(1)–O(3)	177.7(3)
O(4)–Ru(1)–O(3)	90.9(4)	O(2)–Ru(1)–O(3)	89.7(2)
O(1)–Ru(1)–O(1)′	88.7(2)	O(4)–Ru(1)–O(1)′	88.9(3)
O(2)–Ru(1)–O(1)′	88.2(2)	O(3)–Ru(1)–O(1)′	99.3(3)
O(1)–Ru(1)–Ru(2)	90.6(2)	O(4)–Ru(1)–Ru(2)	91.3(2)
O(2)–Ru(1)–Ru(2)	91.6(2)	O(3)–Ru(1)–Ru(2)	91.6(2)
O(1)′–Ru(1)–Ru(2)	169.1(2)	Ru(1)–O(1)–Ru(1)	101.5(3)

Symmetry transformations used to generate equivalent atoms.

Finally we call attention to a comparison of certain properties of the three forms of $Ru_2(chp)_4$. Despite the three different regiochemistries, the colors are fairly similar. On the other hand, they differ in their reactivities toward oxygen. Compound **1** in solution is stable towards air for days, whereas the other two are extremely sensitive as indicated by the immediate development of a purple color when solutions are exposed to air.

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