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Mixed-ligand Complexes of Diruthenium(II, III): Syntheses and Molecular Structures of Chloro-bis-(acetato)-bis-(2-anilinopyridinato)(2-anilinopyridine)-diruthenium·methylene Chloride and Chloro-(acetato)-tris(6-chloro-2-oxypyridinato)diruthenium·methylene Chloride

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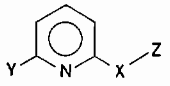
Abstract

The compound $Ru_2Cl(O_2CCH_3)_2(PhNpy)_2(PhNHpy)\cdot CH_2Cl_2$ (**1**) was prepared by reacting $Ru_2Cl(O_2CCH_3)_4$ and PhNHpy (in 1:3 molar proportions) in boiling methanol and crystallized by slow evaporation of a solution of the compound in a CH_2Cl_2–hexane mixture. The compound $Ru_2Cl(O_2CCH_3)(chp)_3\cdot CH_2Cl_2$ (**2**) was obtained in a similar way with a 1:4 molar proportion of starting acetate to Hchp. While **1** is dark blue in color, **2** is purple. Both compounds are soluble in common organic solvents other than hexane and are indefinitely stable in air. Compounds **1** and **2** crystallize in the triclinic space group $P\bar{1}$ and the orthorhombic space group *Pnma*, respectively, with the following unit cell dimensions: **1**, a = 12.093(2) Å, b = 12.143(3) Å, c = 14.357(3) Å, α = 94.94(2)°, β = 114.15(2)°, γ = 92.01(2)°, V = 1911(1) Å^3, and Z = 2; **2**, a = 16.912(5) Å, b = 15.975(4) Å, c = 10.329(6) Å, V = 2791(2) Å^3, and Z = 4. The structures of **1** and **2** were refined to R = 0.044 (R_w = 0.062) and R = 0.058 (R_w = 0.066), respectively. In **1**, the diruthenium(II, III) unit is bridged by two acetate and two 2-anilinopyridine anionic ligands (both oriented in the same direction) in *trans*-disposition. The axial positions are occupied by a Cl anion and a neutral PhNHpy ligand. The metal atom bonded to two equatorial pyridine nitrogen atoms has the Cl axial coordination. The amine hydrogen atom of the other axial ligand is hydrogen bonded to one bridging acetate group. The Ru–Ru, Ru–Cl and Ru–N(axial) distances in **1** are 2.308(1) Å, 2.560(2) Å, and 2.457(6) Å, respectively. The Ru–N (equatorial) and Ru–O distances are in the ranges 2.024(5)–2.098(6) Å and 2.030(5)–2.055(4) Å, respectively. In **2**, a polar arrangement of three bridging chp ligands around the diruthenium(II, III) unit is also present, along with one bridging $CH_3CO_2^-$ ligand. The ruthenium atom which is bonded to four oxygen atoms has an axially coordinated Cl ion. The axial site of the other ruthenium atom, which is bonded to three N and one O atoms, is empty because of the three Cl atoms of the chp ligands that project into this axial site. The Ru–Ru and Ru–Cl distances in **2** are 2.282(4) Å and 2.474(9) Å, respectively. The Ru–N and Ru–O distances lie in the ranges 2.06(2)–2.11(2) Å and 1.95(2)–2.03(2) Å, respectively. Electronic spectra of the solutions of **1** and **2** in CH_2Cl_2 display bands at 695 nm (ϵ = 6560 M^{-1} cm^{-1}) and 535 nm (ϵ = 3990 M^{-1} cm^{-1}), respectively.

Introduction

One present objective in the chemistry of metal–metal multiple bonds is to synthesize new dimeric species having short metal–metal bonds. When the M–M core is spanned by bridging ligands, the steric properties of those ligands play a significant role in stabilizing the dimeric unit [1]. Besides carboxyl groups, the ligands which have been extensively used [1] for this purpose are of the type **I**.



I

	X	Y	Z	
(a)	O	H	H	Hhp
(b)	O	CH_3	H	Hmhp
(c)	O	Cl	H	Hchp
(d)	O	F	H	Hfhp
(e)	NH	H	H	Hap
(f)	NH	H	C_6H_5	PhNHpy

Until quite recently, the only known [2–6] diruthenium complexes having Ru–Ru multiple bonds

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were tetracarboxylato species of the type $Ru_2Cl(O_2CR)_4$. Recent additions [7–10] to these are the tetraamidato complexes $Ru_2Cl(HNOCR)_4$. Structural studies [3–6, 8] done on both these classes of complexes show that the Ru–Ru core is bridged by four O_2CR or HNOCR groups. The $Ru_2(O_2CR)_4^+$ or $Ru_2(HNOCR)_4^+$ units are then linked by terminal chloride ions in infinite chains, some linear and others zigzag. The formal oxidation state of the metal is non-integral, + 2.5. While the Ru–Ru bonds in these complexes are strong, the Ru–Cl bonds that link the Ru_2 units into chains are weak and readily cleaved in polar solvents [4, 7, 9]. Magnetic moments indicating the presence of three unpaired electrons are due to near degeneracy of the π^* and δ^* orbitals, thus giving a ground electronic configuration [11] of $(\sigma)^2(\pi)^4(\delta)^2(\pi^*)^2(\delta^*)^1$. The complexes are extremely stable compared to some recently discovered Ru(II)Ru(II) [12–15] and Ru(III)Ru(III) [13, 16] complexes.

The first attempt to use the type **I** ligand in diruthenium chemistry was made [15] by Garner, Clegg and coworkers in 1981. From the reaction between $Ru_2Cl(O_2CCH_3)_4$ and Na(mhp) in CH_3OH at room temperature under a dinitrogen atmosphere, they were able to isolate an air-sensitive product, $Ru_2(mhp)_4 \cdot CH_2Cl_2$, in *ca.* 8% yield [15]. Our previous experience shows that $Ru_2Cl(O_2CCH_3)_4$ when reacted with the lithium or sodium salt of an anionic ligand, readily looses the terminal chloride ion and the product is an intractable mixture. For instance, the reaction between $Ru_2Cl(O_2CCH_3)_4$ and Li(ap) does not yield any clean product but when the reaction mixture is further treated with PMe_2Ph one obtains $Ru_2(ap)_6(PMe_2Ph)_2$ in which the ligand ap exhibits three different coordination modes [17]. Later on, by using the ligand as such (rather than an alkali metal salt) but varying the experimental conditions we have been able to isolate a large number of diruthenium(II, III) complexes [18–22]. The idea of using the free ligand has proved effective not only in the synthesis of new diruthenium species but also in the preparation of diosmium complexes [23].

The reactions between $Ru_2Cl(O_2CCH_3)_4$ and molten Hhp, Hchp, Hfhp and PhNHpy have given [18, 19, 22] products $Ru_2Cl(hp)_4(Hhp)$, $Ru_2Cl(chp)_4 \cdot CH_2Cl_2$, $Ru_2Cl(fhp)_4$ and $Ru_2Cl(PhNpy)_4$, respectively. Structural studies done on these II, III complexes show a totally polar arrangement of ligands (*i.e.*, all pointing one way) around the diruthenium unit, and all are discrete dimeric species. Only in the **II**, **II** complex, $Ru_2(mhp)_4 \cdot CH_2Cl_2$, is the arrangement [15] of ligands of the more usual 2:2 type.

Our attempts to prepare a polar $Ru_2Cl(mhp)_4$ by a melt reaction were unsuccessful, but we have been able to isolate a mixed-ligand complex $Ru_2Cl(O_2CCH_3)_2(mhp)_2 \cdot 0.5CH_2Cl_2$, the first mixed ligand complex in diruthenium chemistry, from the reaction between $Ru_2Cl(O_2CCH_3)_4$ and Hmhp in boiling methanol. We were interested to explore the reactivity of $Ru_2Cl(O_2CCH_3)_4$ towards other type **I** ligands in methanol. The results of our investigations which yield two more, new, mixed-ligand complexes of diruthenium(II, III), $Ru_2Cl(O_2CCH_3)_2(PhNpy)_2(PhNHpy) \cdot CH_2Cl_2$ (**1**) and $Ru_2Cl(O_2CCH_3)(chp)_3 \cdot CH_2Cl_2$ (**2**), are reported in this paper. In addition to the syntheses, the molecular structures of **1** and **2** are also presented.

Experimental

$Ru_2Cl(O_2CCH_3)_4$ was prepared [2] by using a literature procedure. The 6-chloro-2-hydroxypyridine (Hchp) and 2-anilinopyridine (PhNHpy) were purchased from Aldrich Chemical Company. Electronic spectra were obtained from a Cary 17D spectrophotometer.

Preparation of $Ru_2Cl(O_2CCH_3)_2(PhNpy)_2(PhNHpy) \cdot CH_2Cl_2$ (1)

0.10 g (*ca.* 0.21 mmol) of $Ru_2Cl(O_2CCH_3)_4$ was added to 15 ml of methanol. The mixture was heated to reflux for 0.5 h and then cooled to room temperature. A 0.095 g (*ca.* 0.6 mmol) quantity of PhNHpy was added to the cold solution and the mixture was refluxed for a further 4 h. The color of the solution was blue. After removing the solvent, the residue was dissolved in 15 ml CH_2Cl_2 and filtered. A 7 ml portion of the filtrate was layered with 10 ml hexane. Slow diffusion of the solvents did not yield any solid, but slow evaporation of the resulting solution gave dark blue crystals suitable for X-ray diffraction studies. The compound is soluble in common organic solvents other than hexane. The isolated yield of the crystalline mass was *ca.* 25%. The electronic spectrum obtained from a blue CH_2Cl_2 solution showed bands at 695 nm (ϵ = 6560 M^{-1} cm^{-1}), and 420 nm (ϵ = 2160 M^{-1} cm^{-1}) along with a shoulder at 600 nm.

Preparation of $Ru_2Cl(O_2CCH_3)(chp)_3 \cdot CH_2Cl_2$ (2)

0.12 g (0.25 mmol) of $Ru_2Cl(O_2CCH_3)_4$ was added to 20 ml of methanol. The mixture was stirred for 1 h. A 0.13 g (1 mmol) quantity of Hchp was added to the solution, which was then heated to reflux for 24 h. The solution, now purple in color, was filtered and the filtrate was evaporated to dryness. The solid purple mass was dissolved in 20 ml CH_2Cl_2–hexane mixture in 1:1 (V:V) proportions. The solution was then allowed to undergo slow evaporation. After several days, deep purple crystals suitable for X-ray diffraction were obtained *ca.* 50% yield. The crystals were of irregular shape and brittle. The electronic spectrum of a purple solution of the compound in CH_2Cl_2 solvent displayed a band at 535 nm (ϵ = 3990 M^{-1} cm^{-1}) and two shoulders at 445 nm and 380 nm.

TABLE I. Crystallographic Data.

Formula	$Ru_2Cl_3O_4N_6C_{38}H_{36}$ (1)	$Ru_2Cl_6O_5N_3C_{18}H_{14}$ (2)
Formula weight	949.25	767.19
Space group	$P\bar{1}$	*Pnma*
Systematic absences	None	$0kl$: $k + l = 2n$; $hk0$: $h = 2n$ $h00$: $h = 2n$; $0k0$: $k = 2n$; $00l$: $l = 2n$
a, Å	12.093(2)	16.912(5)
b, Å	12.143(3)	15.975(4)
c, Å	14.357(3)	10.329(6)
α, degrees	94.94(2)	90.0
β, degrees	114.15(2)	90.0
γ, degrees	92.01(2)	90.0
V, Å^3	1911(1)	2791(2)
Z	2	4
D_{calc}, g/cm^3	1.65	1.83
Crystal size, mm	0.5 × 0.5 × 0.2	0.4 × 0.2 × 0.2
μ(Mo-Kα), cm^{-1}	10.34	16.75
Data collection instrument	Nicolet P3	Nicolet P3
Radiation (monochromated in incident beam)	Mo (Kα = 0.71073 Å)	Mo (Kα = 0.71073 Å)
Orientation reflections, number, range (2θ)	25, $20.7° < 2\theta < 29.2°$	25, $15° < 2\theta < 25°$
Temperature, °C	22 ± 1	22 ± 1
Scan method	$\omega - 2\theta$	$\omega - 2\theta$
Data col. range, 2θ, deg.	$4° \leq 2\theta \leq 50°$	$4° \leq 2\theta \leq 45°$
No. unique data, total	5782	1327
with $F_o^2 > 3\sigma(F_o^2)$	4151	639
Number of parameters refined	482	122
Trans. factors, max., min.	99.98%, 82.90%	99.51%, 73.09%
R[a]	0.044	0.058
R_w[b]	0.062	0.066
Quality-of-fit indicator[c]	1.27	1.26
Largest shift/e.s.d., final cycle	0.28	0.29
Largest peak, e/Å^3	0.69	1.08

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality of fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{parameters})]^{1/2}$.

X-ray Crystallographic Procedures

The structures of **1** and **2** were determined by following general procedures described elsewhere [24].* A detailed description of the crystal structure determinations is available as supplementary material. The crystal parameters and basic information pertaining to data collection and structure refinement are summarized in Table I.

Compound **1** forms dark blue crystals in the triclinic system, space group $P\bar{1}$, with the entire molecule as the crystallographic asymmetric unit. The positions of the metal atoms were obtained from a three-dimensional Patterson map. At first the two dimers were located and refined in space group $P1$, but a change was then made to $P\bar{1}$, in which the remainder of the structure was located and refined. The crystals of **1** were of very good diffraction quality and there was no decay of the crystal during 170.9 h exposure time during data collection.

The brittle, purple crystals of **2** were irregular in shape and were found to lose crystallinity when mounted on a fiber with epoxy cement. Attempts to mount the crystal inside a capillary with mother liquor were unsuccessful because of the brittleness of the crystal. Finally, after several attempts, a crystal was found that continued to diffract even when mounted on a fiber with epoxy cement, although gradual deterioration occurred. Data were collected from this crystal at a fast rate, with a 36.7% decay of the crystal during 94.1 h exposure time. Only 1327 unique data in which 639 were above 3σ were obtained. The crystals belong to the orthorhombic space

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*Calculations were done on the VAX-11/780 computer at the Department of Chemistry, Texas A & M University, College Station, Texas with a VAX-SDP software package.

group *Pnma*. The position of the metal atom was obtained from direct methods program MULTAN. The remainder of the structure was solved by use of difference Fourier maps and least-squares refinements. Few atoms were refined anisotropically because of the scarcity of data. The presence of a CH_2Cl_2 molecule as solvent of crystallization is probably the source of the problems during the data collection. Despite these problems, the structure refined well as can be judged from the values of residuals, largest shift/esd ratio, and the quality-of-fit indicator (Table I).

Results and Discussion

Synthetic Aspects

Earlier reports from this laboratory showed [18, 19, 21, 22] that $Ru_2Cl(O_2CCH_3)_4$ when reacted with molten ligands of type I yields totally substituted compounds with Hhp, Hchp, Hfhp and PhNHpy. Although heating the starting acetate compound with an excess of the molten ligands could be considered as rather drastic, the products from those reactions are obtained pure and in quantitative yield. Ligands having bulky X or Z substituents *e.g.* Hchp, Hfhp and PhNHpy, are found to give polar compounds $Ru_2Cl(NX)_4$ in which the orientation of the bridging ligands are unidirectional and as a result one axial site of the diruthenium(II, III) core is blocked by four bulky X or Z groups projected along the axial site. The less hindered axial position is occupied by a Cl ion. The situation [18] is quite different for the Hhp complex, $Ru_2Cl(hp)_4(Hhp)$. Since this ligand does not impose any steric constraints, both the axial sites are occupied, one by a Cl ion and the other by a neutral Hhp ligand. The most surprising thing in this molecule is the presence of a polar arrangement of the hp ligands.

Attempts to prepare $Ru_2Cl(mhp)_4$ using a similar synthetic route were unsuccessful. Structural studies [19] done on $Ru_2Cl(chp)_4 \cdot CH_2Cl_2$ show that the formation of $Ru_2Cl(mhp)_4$ would be difficult, if not impossible. While investigating the reactivity of type I ligands with $Ru_2Cl(O_2CCH_3)_4$ we were aware of the results reported [15] earlier by Garner, Clegg and coworkers. From a reaction between $Ru_2Cl(O_2CCH_3)_4$ and Na(mhp) in methanol at room temperature under a dinitrogen atmosphere they were able to isolate the compound $Ru_2(mhp)_4 \cdot CH_2Cl_2$, but in only 8% yield. Under aerobic condition, by boiling a methanol solution of $Ru_2Cl(O_2CCH_3)_4$ and Hmhp we have been able to isolate a mixed-ligand complex $Ru_2Cl(O_2CCH_3)_2(mhp)_2 \cdot 0.5CH_2Cl_2$ in almost quantitative yield [20]. Using similar reaction conditions it is observed that when $Ru_2Cl(O_2CCH_3)_4$ and PhNHpy were reacted in 1:4 molar proportions, the product is the already reported green $Ru_2Cl(PhNpy)_4$. On changing the molar proportions from 1:4 to 1:3, a blue solution was obtained. The homogeneous crystalline mass obtained after slow evaporation of a solution of the compound in CH_2Cl_2–hexane mixture was found from single crystal X-ray diffraction studies to be $Ru_2Cl(O_2CCH_3)_2(PhNpy)_2(PhNHpy) \cdot CH_2Cl_2$ (**1**). Another mixed-ligand complex, $Ru_2Cl(O_2CCH_3)(chp)_3 \cdot CH_2Cl_2$ (**2**), was obtained from a similar reaction by using $Ru_2Cl(O_2CCH_3)_4$ and Hchp in 1:4 molar proportions.

The electronic spectrum of the blue solution of **1** in CH_2Cl_2 exhibits a strong band at 695 nm (ϵ = 6560 M^{-1} cm^{-1}). A similar absorption is known [18] to occur in $Ru_2Cl(PhNpy)_4$ at 764 nm (ϵ = 6910 M^{-1} cm^{-1}). The observed shift in band positions is *ca.* 1300 cm^{-1}. The electronic spectrum of the purple solution of **2** in CH_2Cl_2 displays a band at 535 nm (ϵ = 3990 M^{-1} cm^{-1}). The absorption bands observed in $Ru_2Cl(chp)_4$, $Ru_2Cl(fhp)_4$ and $Ru_2Cl(O_2CCH_3)_2(mhp)_2$ are at 536 nm (ϵ = 4740 M^{-1} cm^{-1}), 522 nm (ϵ = 4740 M^{-1} cm^{-1}) and 550 nm (ϵ = 3370 M^{-1} cm^{-1}), respectively. A considerable shift of the band position is observed [18] in $Ru_2Cl(hp)_4(Hhp)$ in which the absorption occurs at 480 nm (ϵ = 4690 M^{-1} cm^{-1}). The electronic spectra of compounds **1** and **2** are shown in Fig. 1. Besides the prominent band there are also some other bands and shoulders. In **1**, two more absorptions are observed at 420 nm (ϵ = 2160 M^{-1} cm^{-1}) and 600 nm (shoulder). Compound **2** displays two shoulders at 445 nm and 380 nm.

The low-energy band in **1** and **2** may be attributed [11] to an allowed charge-transfer transition involving ligand (π) and RuRu (π^*) orbitals. The evidence for this tentative assignment is the observed

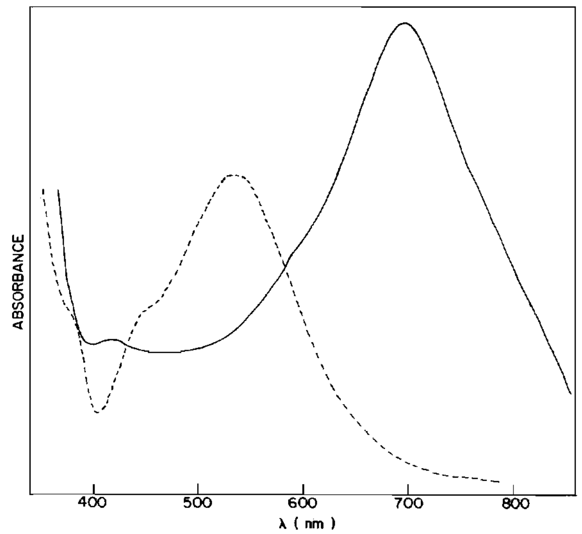


Fig. 1. Electronic Spectra of $Ru_2Cl(O_2CCH_3)_2(PhNpy)_2(PhNHpy) \cdot CH_2Cl_2$ (———) and $Ru_2Cl(O_2CCH_3)(chp)_3 \cdot CH_2Cl_2$ (– – –) in CH_2Cl_2.

TABLE II. Table of Positional Parameters and their e.s.d.s for $Ru_2Cl(OAc)_2(PhNpy)_2(PhNHpy){\cdot}CH_2Cl_2$.

Atom	*x*	*y*	*z*	*B(A2)*
Ru1	0.15002(4)	0.22597(5)	0.36138(4)	2.36(1)
Ru2	0.26524(5)	0.25269(5)	0.26961(4)	2.37(1)
Cl1	0.0089(2)	0.1991(2)	0.4519(1)	4.55(4)
Cl2	−0.3282(3)	0.0647(2)	0.4215(3)	7.44(9)
Cl3	−0.3078(4)	−0.0837(4)	0.2658(3)	12.1(1)
O1	−0.0016(4)	0.2480(4)	0.2318(3)	3.1(1)
O2	0.4142(4)	0.2203(4)	0.3962(3)	3.2(1)
O3	0.3023(4)	0.2007(4)	0.4858(3)	3.1(1)
O4	0.1116(4)	0.2814(4)	0.1455(3)	3.0(1)
N1	0.2324(5)	0.0904(5)	0.2137(4)	2.9(1)
N2	0.1313(5)	0.0553(5)	0.3143(4)	2.9(1)
N3	0.2914(5)	0.4177(5)	0.3187(4)	2.7(1)
N4	0.1805(5)	0.3948(5)	0.4145(4)	2.8(1)
N5	0.4018(5)	0.2765(5)	0.1835(4)	3.2(1)
N6	0.2562(5)	0.3299(6)	0.0355(4)	3.5(1)
C1	0.0086(6)	0.2665(6)	0.1506(5)	3.0(2)
C2	−0.1045(7)	0.2723(8)	0.0540(6)	4.4(2)
C3	0.4029(6)	0.2005(6)	0.4783(5)	3.0(2)
C4	0.5148(7)	0.1748(7)	0.5679(6)	4.2(2)
C5	−0.2323(9)	−0.0165(9)	0.3851(8)	6.3(3)
C11	0.2577(6)	0.0505(6)	0.1269(5)	3.4(2)
C12	0.3685(7)	0.0044(8)	0.1438(6)	4.7(2)
C13	0.3912(8)	−0.0378(8)	0.0604(7)	5.7(2)
C14	0.3066(9)	−0.0274(9)	−0.0393(7)	6.1(2)
C15	0.1964(9)	0.0218(8)	−0.0560(6)	5.3(2)
C16	0.1734(8)	0.0599(7)	0.0278(6)	4.2(2)
C21	0.1763(6)	0.0160(6)	0.2463(5)	3.2(2)
C22	0.1642(7)	−0.0996(6)	0.2149(6)	4.0(2)
C23	0.1071(8)	−0.1734(7)	0.2525(7)	4.9(2)
C24	0.0613(8)	−0.1315(8)	0.3244(6)	5.1(2)
C25	0.0757(7)	−0.0185(7)	0.3518(6)	3.8(2)
C31	0.3575(6)	0.4918(6)	0.2841(5)	3.1(2)
C32	0.4840(6)	0.5047(7)	0.3333(6)	3.8(2)
C33	0.5477(7)	0.5724(8)	0.2971(7)	4.7(2)
C34	0.4879(8)	0.6300(8)	0.2124(6)	4.9(2)
C35	0.3604(8)	0.6201(8)	0.1646(6)	4.8(2)
C36	0.2961(7)	0.5496(7)	0.1985(6)	3.6(2)
C41	0.2458(6)	0.4640(6)	0.3824(5)	2.7(1)
C42	0.2663(7)	0.5803(6)	0.4176(5)	3.5(2)
C43	0.2221(7)	0.6209(7)	0.4896(6)	3.8(2)
C44	0.1601(7)	0.5480(7)	0.5262(5)	3.6(2)
C45	0.1418(6)	0.4371(6)	0.4872(5)	3.2(2)
C51	0.3764(6)	0.3143(7)	0.0923(5)	3.2(2)
C52	0.4690(7)	0.3405(9)	0.0597(6)	5.4(2)
C53	0.5854(8)	0.321(1)	0.1187(7)	6.6(3)
C54	0.6118(7)	0.2747(9)	0.2128(7)	5.4(2)
C55	0.5174(7)	0.2554(7)	0.2423(6)	4.0(2)
C61	0.2025(6)	0.3627(6)	−0.0629(5)	3.3(2)
C62	0.2354(8)	0.3164(9)	−0.1404(6)	5.4(2)
C63	0.1729(9)	0.351(1)	−0.2417(7)	6.7(3)
C64	0.0822(8)	0.4245(9)	−0.2618(7)	5.8(2)
C65	0.0472(9)	0.4586(8)	−0.1863(7)	5.7(3)
C66	0.1064(8)	0.4288(8)	−0.0861(7)	5.0(2)
H6	0.213(6)	0.313(6)	0.064(5)	4(2)[a]

[a] Refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $4/3\,[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab\,(\cos\gamma)\beta_{12} + ac\,(\cos\beta)\beta_{13} + bc\,(\cos\alpha)\beta_{23}]$.

TABLE III. Table of Positional Parameters and their e.s.d. s for $Ru_2Cl(O_2CCH_3)(chp)_3 \cdot CH_2Cl_2$ (2).

Atom	*x*	*y*	*z*	*B(A2)*
Ru1	0.6947(2)	0.250	0.5549(3)	2.30(5)
Ru2	0.7009(2)	0.250	0.3343(3)	2.57(6)
Cl1	0.8113(6)	0.250	0.809(1)	6.3(3)
Cl2	0.6525(5)	0.1324(4)	0.7960(7)	5.3(2)
Cl3	0.6993(6)	0.250	0.0947(7)	3.0(2)
Cl4	0.4854(5)	−0.0427(7)	0.750(1)	10.2(3)
Cl5	0.3861(5)	0.0411(5)	0.930(1)	8.0(3)
O1	0.816(1)	0.250	0.337(2)	3.4(5)[a]
O2	0.7010(9)	0.1255(9)	0.331(1)	3.4(3)[a]
O3	0.575(1)	0.250	0.549(2)	2.9(4)[a]
O4	0.583(1)	0.250	0.329(2)	3.6(5)[a]
N1	0.820(1)	0.250	0.555(3)	2.3(5)[a]
N2	0.691(1)	0.121(1)	0.553(2)	2.8(4)
C1	0.858(2)	0.250	0.447(4)	4.1(8)[a]
C2	0.941(2)	0.250	0.438(4)	3.5(7)[a]
C3	0.984(2)	0.250	0.552(4)	3.7(7)[a]
C4	0.946(2)	0.250	0.671(4)	5(1)[a]
C5	0.868(2)	0.250	0.664(3)	3.1(7)[a]
C6	0.697(1)	0.080(1)	0.442(2)	3.3(4)[a]
C7	0.693(1)	−0.010(1)	0.428(2)	4.3(5)[a]
C8	0.684(1)	−0.052(1)	0.540(2)	3.9(5)[a]
C9	0.673(1)	−0.012(2)	0.666(2)	4.1(6)[a]
C10	0.675(1)	0.076(2)	0.658(2)	3.8(6)[a]
C11	0.541(2)	0.250	0.434(4)	3.9(8)[a]
C12	0.452(2)	0.250	0.437(4)	6(1)[a]
C13	0.422(2)	−0.057(2)	0.880(3)	5.9(8)[a]

[a] Refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab\ (\cos\gamma)\beta_{12} + ac\ (\cos\beta)\beta_{13} + bc\ (\cos\alpha)\beta_{23}]$.

shift of the band positions on changing O,O (carboxylato) to O,N (hydroxypyridines) to N,N (anilinopyridine) ligand coordination.

Molecular Structures

The positional and thermal parameters for compounds 1 and 2 are presented in Tables II and III, respectively. Tables IV and V list selected bond distances and angles for 1 and 2, respectively. ORTEP drawings of the molecules in 1 and 2 along with the atom labelling scheme are shown in Figs. 2 and 3, respectively.

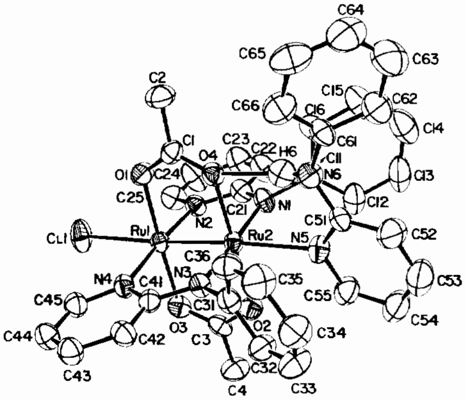


Fig. 2. ORTEP view of the complex molecule in $Ru_2Cl(O_2CCH_3)_2(PhNpy)_2(PhNHpy) \cdot CH_2Cl_2$ with atom labeling scheme.

Compound 1

This crystallizes in the triclinic space group $P\bar{1}$ with one complete complex and one CH_2Cl_2 molecule in the crystallographic asymmetric unit. The diruthenium(II, III) unit in 1 is bridged by two acetate and two PhNpy ligands in *trans* disposition. The coordination geometry of each metal atom is pseudooctahedral. The atom Ru(1) is bonded to two equatorial pyridine nitrogen atoms, two equatorial acetate oxygen atoms and to one axial Cl atom with a coordination sphere of Ru(2)Cl(1)O(1)O(3)N(2)(N4). The coordination environment of Ru(2) is comprised of Ru(1)O(2)O(4)N(1)N(3)N(5) in which N(1) and N(3) are amine nitrogen atoms of bridging PhNpy ligands while N(5) is the axial pyridine nitrogen atom. The axial coordination to Ru(2) is by a neutral PhNHPy ligand. The amine proton of this ligand was located from difference Fourier maps and refined isotropically along with other atoms. As can be seen from Fig. 1 and Table IV, the H(6) atom is engaged

TABLE IV. Some Important Bond Distances (Å) and Angles (degree) in $Ru_2Cl(O_2CCH_3)_2(PhNpy)_2(PhNHpy)\cdot CH_2Cl_2$ (**1**)[a].

Bond Distances	
Ru(1)–Ru(2)	2.308(1)
Ru(1)–Cl(1)	2.560(2)
Ru(1)–O(1)	2.055(4)
Ru(1)–O(3)	2.030(5)
Ru(1)–N(2)	2.098(6)
Ru(1)–N(4)	2.091(6)
Ru(2)–O(2)	2.049(5)
Ru(2)–O(4)	2.047(5)
Ru(2)–N(1)	2.024(5)
Ru(2)–N(3)	2.035(5)
Ru(2)–N(5)	2.457(6)
C(1)–O(1)	1.258(8)
C(1)–O(4)	1.286(8)
C(3)–O(2)	1.283(8)
C(3)–O(3)	1.264(8)
C(11)–N(1)	1.450(8)
C(21)–N(1)	1.335(9)
C(21)–N(2)	1.360(9)
C(31)–N(3)	1.430(8)
C(41)–N(3)	1.343(8)
C(41)–N(4)	1.364(8)
C(61)–N(6)	1.393(9)
C(51)–N(6)	1.375(9)
C(51)–N(5)	1.343(8)
N(6)–H(6)	0.82(8)
O(4)–H(6)	2.055
O(4)–N(6)	2.872
Cl(2)–C(5)	1.754(11)
Cl(3)–C(5)	1.691(11)
Bond Angles	
Ru(2)–Ru(1)–Cl(1)	175.91(6)
Ru(2)–Ru(1)–O(1)	88.2(1)
Ru(2)–Ru(1)–O(3)	90.0(1)
Ru(2)–Ru(1)–N(2)	89.4(2)
Ru(2)–Ru(1)–N(4)	89.5(2)
Ru(1)–Ru(2)–O(4)	89.8(1)
Ru(1)–Ru(2)–N(1)	90.1(2)
Ru(1)–Ru(2)–O(2)	87.9(1)
Ru(1)–Ru(2)–N(3)	90.5(2)
Ru(1)–Ru(2)–N(5)	175.4(2)
Cl(1)–Ru(1)–O(1)	87.7(1)
Cl(1)–Ru(1)–O(3)	94.1(2)
Cl(1)–Ru(1)–N(2)	90.9(2)
Cl(1)–Ru(1)–N(4)	90.5(2)
N(5)–Ru(2)–O(2)	87.5(2)
N(5)–Ru(2)–O(2)	87.5(2)
N(5)–Ru(2)–O(4)	94.8(2)
N(5)–Ru(2)–N(1)	89.6(2)
N(5)–Ru(2)–N(3)	90.1(2)
O(1)–Ru(1)–O(3)	177.7(2)
O(1)–Ru(1)–N(2)	90.1(2)
O(3)–Ru(1)–N(2)	88.4(2)
N(2)–Ru(1)–N(4)	176.3(2)
O(2)–Ru(2)–O(4)	177.5(2)
O(2)–Ru(2)–N(1)	91.5(2)
O(2)–Ru(2)–N(3)	91.4(2)
O(4)–Ru(2)–N(1)	87.5(2)
O(4)–Ru(2)–N(3)	89.5(2)
N(1)–Ru(2)–N(3)	177.0(2)
Ru(1)–O(1)–C(1)	120.2(4)
Ru(2)–O(4)–C(1)	118.2(4)
Ru(1)–O(3)–C(3)	119.2(4)
Ru(2)–O(2)–C(3)	120.0(5)
Ru(2)–N(1)–C(11)	120.7(4)
Ru(2)–N(1)–C(21)	123.3(5)
Ru(1)–N(2)–C(21)	119.8(5)
Ru(2)–N(3)–C(31)	121.2(4)
Ru(2)–N(3)–C(41)	122.7(5)
Ru(1)–N(4)–C(41)	120.4(5)
Ru(2)–N(5)–C(51)	128.0(5)
O(1)–C(1)–O(4)	123.2(6)
O(2)–C(3)–O(3)	122.8(6)
N(1)–C(21)–N(2)	116.8(6)
N(3)–C(41)–N(4)	116.9(6)
N(5)–C(51)–N(6)	115.7(6)
C(51)–N(6)–C(61)	128.5(6)
C(51)–N(6)–H(6)	113(6)
C(61)–N(6)–H(6)	119(6)
N(6)–H(6)–O(4)	174.9
Cl(2)–C(5)–Cl(3)	111.3(6)

[a] Numbers in parentheses are e.s.d.s in the least significant digits.

in hydrogen-bonding with the acetate oxygen atom, O(4). The O(4)–H(6), N(6)–H(6), and O(4)–N(6) distances in **1** (of which the first two are not individually reliable) are 2.06(8) Å, 0.82(8) Å and 2.87(1) Å. A similar sort of H-bonding is also present [18] in the $Ru_2Cl(hp)_4(Hhp)$ molecule, in which the H–O, H–N and O–N distances are 1.89 Å, 0.95 Å, and 2.78 Å, respectively. The N(6)–H(6)–O(4) angle in **1** is almost linear, 174.9°.

The orientation of the PhNpy ligands in **1** is unidirectional. In a closely related system $Ru_2Cl(PhNpy)_4$ [18], a unidirectional arrangement of all four PhNpy ligands around the diruthenium core was observed. In this molecule the ruthenium atom that is bonded to four amine nitrogen atoms has a vacant axial site because of the blocking effect of the four pendant phenyl groups along the Ru–Ru axis. In **1** though two phenyl groups are present near the Ru(2) atom, there is room for axial coordination by utilizing the plane perpendicular to the N(1)–Ru(2)–N(3) axis. The flexibility of the phenyl groups is also responsible for making the axial coordination on Ru(2) possible. The situation can be compared [20] to that in the reported mixed-ligand species $Ru_2Cl(O_2CCH_3)_2(mhp)_2\cdot 0.5CH_2Cl_2$. The 6-methyl groups of two mhp ligands effectively block one axial site because of the steric rigidity of the ligand system.

The Ru(1)–Ru(2) distance in **1** is 2.308(1) Å. In $Ru_2Cl(PhNpy)_4$ [18], and $Ru_2Cl(O_2CCH_3)_4$ [6], the Ru–Ru distances are 2.275(3) Å and 2.287(2) Å, respectively. The considerable increase in the Ru–Ru distance in **1** could be due to the presence of two

TABLE V. Selected Bond Distances (Å) and Angles (deg.) in $Ru_2Cl(O_2CCH_3)(chp)_3 \cdot CH_2Cl_2$ (**2**)[a].

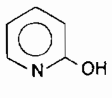
Bond Distances			
Ru(1)–Ru(2)	2.282(4)	O(1)–C(1)	1.35(4)
Ru(1)–O(3)	2.03(2)	N(1)–C(1)	1.29(5)
Ru(1)–N(1)	2.11(2)	O(2)–C(6)	1.36(3)
Ru(1)–N(2)	2.06(2)	N(2)–C(6)	1.32(3)
Ru(2)–Cl(3)	2.474(9)	O(3)–C(11)	1.31(4)
Ru(2)–O(1)	1.95(2)	O(4)–C(11)	1.30(4)
Ru(2)–O(2)	1.99(2)	N(1)–C(5)	1.40(4)
Ru(2)–O(4)	2.00(2)	N(2)–C(10)	1.33(3)
Cl(1)–C(5)	1.78(4)		
Cl(2)–C(10)	1.73(3)		
Cl(4)–C(13)	1.73(3)		
Cl(5)–C(13)	1.76(3)		
Bond Angles			
Ru(2)–Ru(1)–O(3)	90.9(8)	Ru(1)–N(1)–C(1)	121(3)
Ru(2)–Ru(1)–N(1)	87(1)	Ru(1)–N(1)–C(5)	126(3)
Ru(2)–Ru(1)–N(2)	89.4(6)	Ru(1)–N(2)–C(6)	120(2)
Ru(1)–Ru(2)–Cl(3)	176.8(4)	Ru(1)–N(2)–C(10)	122(2)
Ru(1)–Ru(2)–O(1)	92.0(8)	Ru(1)–O(3)–C(11)	118(2)
Ru(1)–Ru(2)–O(2)	91.0(4)	Ru(2)–O(1)–C(1)	123(2)
Ru(1)–Ru(2)–O(4)	89.0(8)	Ru(2)–O(2)–C(6)	121(1)
Cl(3)–Ru(2)–O(1)	91.3(8)	Ru(2)–O(4)–C(11)	121(3)
Cl(3)–Ru(2)–O(2)	89.0(4)	O(1)–C(1)–N(1)	118(4)
Cl(3)–Ru(2)–O(4)	87.8(8)	O(2)–C(6)–N(2)	118(2)
O(3)–Ru(1)–N(1)	178(1)	O(3)–C(11)–O(4)	121(3)
O(3)–Ru(1)–N(2)	88.3(6)	N(1)–C(5)–Cl(1)	111(3)
N(1)–Ru(1)–N(2)	91.6(6)	N(2)–C(10)–Cl(2)	116(2)
O(1)–Ru(2)–O(2)	89.9(5)	Cl(4)–C(13)–Cl(5)	109(2)
O(1)–Ru(2)–O(4)	179.1(9)		
O(2)–Ru(2)–O(4)	90.0(5)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

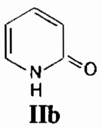
axial coordinations, one of which is a neutral PhNHpy ligand that can act as a good π-acceptor ligand. A similar lengthening effect is also observed among 2-hydroxypyridine complexes. The Ru–Ru bond lengths in $Ru_2Cl(hp)_4(Hhp)$ [18], $Ru_2Cl(chp)_4 \cdot CH_2Cl_2$ [19], $Ru_2Cl(fhp)_4$ [22], and $Ru_2Cl(O_2CCH_3)_2(mhp)_2 \cdot 0.5CH_2Cl_2$ [20] are 2.286(1) Å, 2.281(1) Å, 2.284(1) Å and 2.278(2) Å, respectively. The π-acceptor ability of PhNHpy is more than that of Hhp and thus lengthening effect is more prominent in **1** than in $Ru_2Cl(hp)_4(Hhp)$. The effect in **1** is also enhanced by the essentially planar geometry of the N(6) atom because of the hydrogen bonding (*vide infra*).

The Ru(1)–Cl(1) bond length in **1** is 2.560(2) Å. Among polar compounds having only one axial coordination, the Ru–Cl distance is *ca.* 2.43 Å. In $Ru_2Cl(hp)_4(Hhp)$ molecule, the Ru–Cl distance is 2.558(2) Å. Similarly, in other diruthenium(II, III) complexes with two axial coordinations, such as $Ru_2Cl(O_2CR)_4$ and $Ru_2Cl(4\text{-}Cl\text{–}C_6H_4CONH)_4$, where the diruthenium(II, III) units are linked by Cl ions in an infinite chain [3–6, 8], the Ru–Cl bond lengths also lie in the range 2.52–2.59 Å.

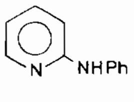
In **1**, the long Ru(1)–Cl(1) bond is accompanied by a long Ru(2)–N(5) bond, 2.457(6) Å, which may be compared to the equatorial Ru(1)–N(pyridine) distances of 2.091(6) Å and 2.098(6) Å. The Ru–N (pyridine) distances found in $Ru_2Cl(PhNpy)_4$ lie in the range 2.102(12)–2.105(11) Å. One notable difference between the structure of **1** and that of $Ru_2Cl(hp)_4(Hhp)$ [18] is that in **1** the axial ligand PhNHpy is coordinated to Ru(2) through a pyridine nitrogen atom while in the hp complex the axial Hhp ligand is coordinated to ruthenium through an oxygen atom. The proton of the Hhp ligand has migrated to the pyridine nitrogen. This observation is not surprising because in the Hhp ligand the tautomeric form **IIb** is preferred while the tautomeric form **IIIb** is not.



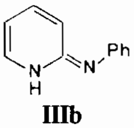
IIa



IIb



IIIa



IIIb

TABLE VI. Comparison of the Torsional Angles in **1**, **2** and Related Species.

Compound	Atom 1	Atom 2	Atom 3	Atom 4	Angle (deg.)
$Ru_2Cl(O_2CCH_3)_2(PhNpy)_2(PhNHpy)\cdot CH_2Cl_2$	O(1)	Ru(1)	Ru(2)	O(4)	2.6
	O(3)	Ru(1)	Ru(2)	O(2)	2.1
	N(2)	Ru(1)	Ru(2)	N(1)	5.2
	N(4)	Ru(1)	Ru(2)	N(3)	−1.3
$Ru_2Cl(O_2CCH_3)(chp)_3\cdot CH_2Cl_2$	N(1)	Ru(1)	Ru(2)	O(1)	0.0
	N(2)	Ru(1)	Ru(2)	O(2)	−1.7
	O(3)	Ru(1)	Ru(2)	O(4)	0.0
$Ru_2Cl(O_2CCH_3)_2(mhp)_2\cdot 0.5CH_2Cl_2$ [a]	O(1)	Ru(1)	Ru(2)	O(2)	0.6
	O(4)	Ru(1)	Ru(2)	O(3)	0.7
	O(11)	Ru(1)	Ru(2)	N(11)	1.3
	O(21)	Ru(1)	Ru(2)	N(21)	2.8
$Ru_2Cl(PhNpy)_4$ [b]	N(2)	Ru(1)	Ru(2)	N(1)	22.8
	N(4)	Ru(1)	Ru(2)	N(3)	22.6
$Ru_2Cl(chp)_4\cdot CH_2Cl_2$ [c]	O(1)	Ru(1)	Ru(2)	N(1)	19.2
	O(2)	Ru(1)	Ru(2)	N(2)	18.4

[a] Ref. [20]. [b] Ref. [18]. [c] Ref. [19].

Among equatorial bonds, the average Ru(2)–N(amine) and Ru(1)–N(pyridine) distances are 2.030(5) Å and 2.094(6) Å, respectively. Assuming the negative charge of the $PhNpy^-$ ligand to be concentrated primarily on the N(amine) atom, it is expected that the Ru–N(pyridine) bonds should be longer than the Ru–N(amine) bonds. In fact, a similar difference in bond lengths is also observed [18] in $Ru_2Cl(PhNpy)_4$.

The Ru(2)–Ru(1)–Cl(1) and Ru(1)–Ru(2)–N(5) angles in **1** are 175.91(6)° and 175.4(2)°, respectively. While the angles Cl(1)–Ru(1)–O(1) and N(5)–Ru(2)–O(2) are acute, being 87.7(1)° and 87.5(2)°, respectively, the angles Cl(1)–Ru(1)–O(3) and N(5)–Ru(2)–O(4) are obtuse, *av.* 94.5(2)°. The observed increase or decrease from 90° can be attributed to the presence of a bulky axial PhNHpy ligand. The angles N(5)–Ru(2)–N(1), N(3) and Cl(1)–Ru(1)–N(2), N(4) are close to 90°. There is a considerable increase in the Ru(2)–N(5)–C(51) angle [128.0(5)°] from the ideal value of 120°. The angles around the N(6) atom are: C(51)–N(6)–C(61), 128.5(6)°; C(51)–N(6)–H(6), 113(6)°; C(61)–N(6)–H(6), 119(6)°, the sum of the three angles being close to 360°. The N(6) atom has thus attained an essential planarity, which is consistent with the short N(6)–C(51), –C(61) bond lengths. These are very close to the N–C distances observed in bridging PhNpy ligands, and indicative of π conjugation.

Earlier, in $Ru_2Cl(PhNpy)_4$ a marked deviation from the eclipsed conformation of the bridging ligands was seen [18] to occur because of crowding due to the proximity of the four phenyl groups; the torsional angles were *ca.* 22.7°. In **1**, the steric strain is largely removed because two PhNpy ligands are replaced by two bridging acetate ligands, and the torsion angles are thus quite small. A list of torsion angles found in **1**, **2** and related species is presented in Table VI. The average torsion angle, O–Ru–Ru–O, of the acetate is *ca.* 2.4°. The extent of torsion in N(2)–Ru(1)–Ru(2)–N(1) is greater than that in N(4)–Ru(1)–Ru(2)–N(3).

Compound 2

This crystallizes in the orthorhombic space group *Pnma*. Structural study shows the presence of the dinuclear molecule $Ru_2Cl(O_2CCH_3)(chp)_3$ and one CH_2Cl_2 molecule as solvent of crystallization in **2**. The complex molecule has a diruthenium(II, III) core bridged by three chp ligands and one acetate ligand, with the arrangement of the chp ligands unidirectional. The coordination geometries of Ru(2) and Ru(1) are pseudooctahedral and square pyramidal, respectively. While Ru(2) has four oxygen atoms in the equatorial positions and Cl(3) in the axial position, Ru(1) is bonded to nitrogen atoms of the chp ligands and one oxygen atom of the acetate. The axial site on Ru(1) is blocked by three 6-chloro atoms of the chp ligands. The complex molecule has a mirror plane as can be seen from the Fig. 3.

The Ru(1)–Ru(2) distance of 2.282(4) Å in **2** is essentially the same as that found [19] in $Ru_2Cl(chp)_4\cdot CH_2Cl_2$. Thus, replacement of one chp by acetate has no effect on the Ru–Ru bond strength. The Ru–Cl distances in **2** and $Ru_2Cl(chp)_4\cdot CH_2Cl_2$ are 2.474(9) Å and 2.443(2) Å, respectively. There is no obvious steric reason for lengthening of the Ru(2)–Cl(3) bond. An even shorter Ru–Cl bond distance, 2.419(5) Å, is found [20] in $Ru_2Cl(O_2CCH_3)_2(mhp)_2\cdot 0.5CH_2Cl_2$. It may be that

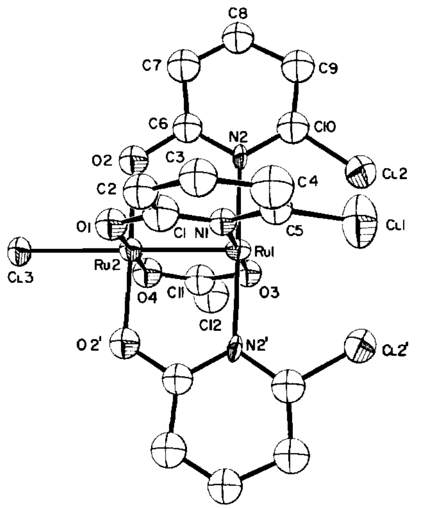


Fig. 3. ORTEP diagram of $Ru_2Cl(O_2CCH_3)(chp)_3$ molecule in 2 along with the atom numbering scheme.

replacement of N atoms in the equatorial set of ligand atoms by the more electronegative oxygen atoms (even though this is occurring at the other metal atom) induces the axial Cl^- ion to function as a better axial ligand. The observed average Ru–N and Ru–O distances in 2 are 2.09(2) Å and 1.98(2) Å, respectively. Similar values are observed [19] in $Ru_2Cl(chp)_4 \cdot CH_2Cl_2$, but in the mhp complex the Ru–O and Ru–N bond lengths are 2.01(1) Å and 2.02(2) Å, respectively. The increase in Ru–N bond length in going from mhp to chp complexes could be due to greater repulsion among the three 6-chloro atoms, as compared to that between two methyl groups. The lengthening of the Ru–N bonds is associated with a shortening of the Ru–O bond lengths. In 2, the angle Ru(1)–Ru(2)–Cl(3) is essentially linear, being 176.8(4)°. The Ru–Ru–O and Ru–Ru–N angles are close to 90°. The N(1)–Ru(2)–N(2) angle is obtuse, 91.6(6)°, while the N(2)–Ru(1)–O(3) angle is acute, 88.3(6)°. This could again be due to steric repulsion between the chp ligands.

The torsional angles found in 2 are presented in Table VI. In the three mixed-ligand complexes, $Ru_2Cl(O_2CCH_3)_2(mhp)_2 \cdot 0.5CH_2Cl_2$, 1 and 2, the bridging ligands are in essentially eclipsed conformation. It is interesting to see that the replacement of the one acetate from 2 by a chp ligand, resulting in $Ru_2Cl(chp)_4 \cdot CH_2Cl_2$, causes [19] a considerable deviation from the eclipsed conformation. The torsion angle found [19] in $Ru_2Cl(chp)_4 \cdot CH_2Cl_2$ is *ca.* 19° (see Table VI). In $Ru_2Cl(chp)_4 \cdot CH_2Cl_2$, the distance between two closest chlorine atoms of the chp ligands is 3.32 Å which is much shorter than the sum of the van der Waals radii of 3.6 Å. The twist observed in this molecule is believed to be due to the close proximity of the Cl atoms. In 2, there is almost no twist in the ligand systems though the distance between Cl(1) and Cl(2) atoms is only 3.28 Å which is shorter than that found [19] in $Ru_2Cl(chp)_4 \cdot CH_2Cl_2$. In 2, the distance between Cl(2) and Cl(2)′ is 3.76 Å.

Conclusions

In the chemistry of metal–metal multiple bonds, the steric properties of a bridging ligand play a significant role in stabilizing the dimeric unit [1]. From our systematic investigations on the reactivity of type I ligands towards $Ru_2Cl(O_2CCH_3)_4$, it is apparent that the steric demands of Y in case of hydroxypyridines and of Z in case of aminopyridines are prominent factors in deciding the stereochemistry as well as the stability of the complexes [18–22]. In diruthenium(II, III) species, the presence of an axial coordination by a Cl ion makes the adoption of the polar arrangement of ligands around the diruthenium core a general phenomenon, irrespective of whether there is considerable strain or no strain in the ligand system in adopting the unidirectional orientation of the ligands.

In the preparation of $Ru_2Cl(O_2CCH_3)_2(mhp)_2 \cdot 0.5CH_2Cl_2$ [20] and 2, the molar proportions used between starting acetate and ligand is 1:4. In one case the result is the substitution of two acetates whereas in 2 we find a replacement of three bridging acetates. The reaction between $Ru_2Cl(O_2CCH_3)_4$ with PhNHpy in 1:3 proportions does not proceed to substitute three acetates. Only two bridging acetates are found to be substituted while the third PhNHpy molecule engages itself in axial ligation, and the overall structure is stabilized by the formation of a hydrogen-bond. When a 1:4 molar ratio is used, the isolated product is the earlier reported [18] $Ru_2Cl(PhNpy)_4$.

Under more forcing experimental conditions (*i.e.*, using the melt reaction proecedure) it is possible to substitute all four acetates except in the case of Hmhp. Using simple Hhp (Y = H), the product isolated [18] is $Ru_2Cl(hp)_4(Hhp)$ which does not have any sort of steric strain and the Ru–Ru unit can undergo axial ligations on both ends through Cl and Hhp. Changing Y = H to Y = F (Hfhp), the product is again a polar compound $Ru_2Cl(fhp)_4$ in which there is only one axial coordination; the other end is blocked by four F atoms [22]. The molecule has a high symmetry and the bridging fhp ligands are in almost eclipsed conformation. When Y = Cl, the product is polar $Ru_2Cl(chp)_4 \cdot CH_2Cl_2$ [19] in which there is strain evidenced by the torsion angle of *ca.* 19°. Using Y = CH_3, the product of the melt reaction is not clean. The formation of polar $Ru_2Cl(mhp)_4$ will need a considerable greater twist in the ligand system than 19° and efforts to isolate this complex have so far failed. Though our study involves primarily the oxypyridonato ligands, the use of 2-anilinopyridine is found [18] to be productive in the preparation of polar compounds. From the melt reaction, the isolated product $Ru_2Cl(PhNpy)_4$ [18] is a polar one having N–Ru–Ru–N torsion angles of *ca.* 22.5°. The amine proton in PhNHpy is acidic enough to undergo cleavage. Other aminopyridines do not seem to be reactive and attempts to prepare similar complexes using the lithium or sodium salt of aminopyridines were unsuccessful. The reaction between $Ru_2Cl(O_2CCH_3)_4$ and Li(ap) in presence of PMe_2Ph is known [17] to produce an edge-sharing bioctahedral species $Ru_2(ap)_6(PMe_2Ph)_2$.

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Supplementary Material Available

Details of the crystal structure determinations and listings of bond angles, anisotropic thermal parameters, bond distances, observed and calculated structure factors, and root-mean-square amplitudes (48 pages). Ordering information is given on any current masthead page.

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