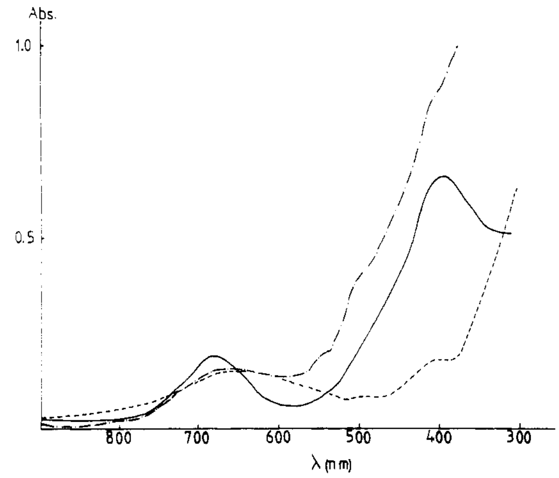

Figure 1. Absorption spectra (concentration of compounds 10^{-4} M): (-•-•) $Os(NO)Cl_2(PPh_3)_2$; (—) $Os(NO)Cl_3(PPh_3)_2$; (---) $Os(NO)Cl(PPh_3)_3$. See text for absorption maxima.

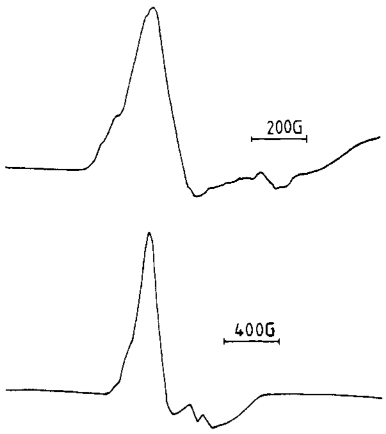

Figure 2. ESR spectra of $Os(NO)Cl_2(PPh_3)_2$ at 295 K: $g_{av} = 2.485$, $g_{\perp} = 2.492$, $g_{\parallel} = 2.481$.

The complex **1** is a nonelectrolyte. Its IR spectrum exhibits ν_{NO} (Table I), $\nu_{OsCl} = 325$ cm^{-1}, and bands due to PPh_3. The magnetic moment for **1** at 22 °C ($\mu = 1.52\ \mu_B$) is lower than the spin-only value. ESR spectra are shown in Figure 2. For a linear $\{MNO\}^7$ system, the unpaired electron could be either in σ_{NO}-d_{z^2} in the case of tetragonal-pyramidal geometry[12] ($g_z \simeq 2.0$), or in $d_{x^2-y^2}$ in the case of distorted-trigonal-bipyramidal geometry ($g_z > 2.0$). The UV/visible spectrum (Figure 1) in benzene shows λ_{max} (ϵ) 805 (5.56), 750 (16.5), 675 (43.5), 555 (52.2), 520 (106), 405 (243), and 275 nm (24124). The lowest energy bands correspond to d → d transitions with the occupied metal orbital having some Cl character. Complex **2** is a nonelectrolyte: ν_{NO} (Table I), $\nu_{OsCl} = 320$ cm^{-1}; $\mu = 1.46\ \mu_B$; ESR ($g_{av} = 2.3495$, $g_{\perp} = 2.4198$, $g_{\parallel} = 2.3136$; UV/visible λ_{max} (ϵ) 810 (13.58), 770 (23.78), 682 (52.3), 560 (120), 515 (136), 390 (308), 278 nm (21062). The corrected ν_{NO} (Table I) falling above 1610 cm^{-1} gives added evidence for the presence of linear nitrosyl groups in these complexes. If the rules that have been suggested by Ibers[14] and Hoffmann et al.[15] for pentacoordinated nitrosyl complexes are combined with empirical rules of stereochemistry, the geometry about the osmium atom is probably a distorted trigonal bipyramid with axial phosphine ligands and two Cl atoms, the NO group occupying the equatorial plane (the molecule has C_{2v} symmetry[16]). These five-coordinated linear $\{OsNO\}^7$ complexes can be regarded as complexes between Os(I) and NO^+.

Complex **3** is a nonelectrolyte, and its solutions are air sensitive: ν_{NO} (Table I), $\nu_{OsCl} = 325$ cm^{-1}; UV/visible λ_{max} (ϵ) 750 (62), 640 (250), 495 (167), 400 (292), 270 nm (41660). Complex **4** is also a nonelectrolyte: ν_{NO} (Table I); UV/visible λ_{max} (ϵ) 755 (65), 640 (162), 515 (286), 400 (315), 275 nm (40980). Complex **4** is more stable in solution than **3**. Complexes **3** and **4** are expected to be distorted trigonal bipyramids with equatorial phosphine ligands and axial NO group trans to X (X = Cl, Br), and the molecules have C_{3v} symmetry.[15]

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Registry No. **1**, 96689-07-5; **2**, 96689-08-6; **3**, 86645-90-1; **4**, 96689-09-7; $OsCl_2(PPh_3)_3$, 40802-32-2; $Os(NO)Cl_3(PPh_3)_2$, 29292-10-2; $Os(NO)Cl_2Br(PPh_3)_2$, 78106-84-0; $Os(NO)Br_3(PPh_3)_2$, 29292-11-3.

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(12) Feltham, R. D.; Enemark, J. H. *Top. Inorg. Organomet. Stereochem.* **1981**, *12*, 155.
(13) Haymore, B. L.; Ibers, J. A. *Inorg. Chem.* **1975**, *14*, 3060.
(14) Haymore, B. L.; Ibers, J. A. *Inorg. Chem.* **1975**, *14*, 2610.
(15) Hoffmann, R.; Chen, M. M. L.; Elian, M.; Rossi, A. R.; Mingos, D. M. P. *Inorg. Chem.* **1974**, *13*, 2666.
(16) Rossi, A. R.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 365.

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Synthesis, Structure, and Properties of Chlorobis(acetato)bis(6-methyl-2-hydroxypyridinato)diruthenium(II,III), the First Ru_2^{5+} Compound with a Mixed Set of Bridging Ligands

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In the chemistry of metal–metal multiple bonds,[1] the oxidation state of the metal center as well as the steric properties of the equatorial and axial ligands plays an important role in determining the coordination geometry and the stability of the complex. Among diruthenium complexes it has been found[2-13] that most of the stable compounds have diruthenium centers with a formal oxidation state of +2.5 for each metal atom. In recent years a few Ru(II)Ru(II)[14-17] and Ru(III)Ru(III)[17,18] complexes have

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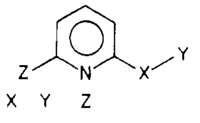
(1) Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982.
(2) Stephenson, T. A.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1966**, *28*, 2285.
(3) Bennett, M. J.; Caulton, K. G.; Cotton, F. A. *Inorg. Chem.* **1969**, *8*, 1.
(4) Bino, A.; Cotton, F. A.; Felthouse, T. R. *Inorg. Chem.* **1979**, *18*, 2599.
(5) (a) Mukaida, M.; Nomura, T.; Ishimori, T. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 2462; **1972**, *45*, 2143. (b) Togano, T.; Mukaida, M.; Nomura, T. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2085.
(6) Martin, D. S.; Newman, R. A.; Vlasnik, L. M. *Inorg. Chem.* **1980**, *19*, 3404.
(7) Wilson, C. R.; Taube, H. *Inorg. Chem.* **1975**, *14*, 2276.
(8) Cotton, F. A.; Pedersen, E. *Inorg. Chem.* **1975**, *14*, 388.
(9) Chavan, M. Y.; Feldman, F. N.; Lin, X. Q.; Bear, J. L.; Kadish, K. M. *Inorg. Chem.* **1984**, *23*, 2373.
(10) Malinski, T.; Chang, D.; Feldman, F. N.; Bear, J. L.; Kadish, K. M. *Inorg. Chem.* **1983**, *22*, 3225.
(11) Chakravarty, A. R.; Cotton, F. A.; Tocher, D. A. *J. Am. Chem. Soc.* **1984**, *106*, 6409.
(12) Chakravarty, A. R.; Cotton, F. A.; Tocher, D. A. Inorg. *Chem.* **1985**, *24*, 172.
(13) Chakravarty, A. R.; Cotton, F. A.; Tocher, D. A. *Inorg. Chem.* **1985**, *24*, 1263.
(14) Berry, M.; Garner, C. D.; Hillier, I. H.; MacDowell, A. A.; Clegg, W. *Inorg. Chim. Acta* **1981**, *53*, L61. Clegg, W. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, *B36*, 3112.
(15) Lindsay, A. J.; Tooze, R. P.; Motevalli, M.; Hursthouse, M. B.; Wilkinson, G. *J. Chem. Soc., Chem. Commun.* **1984**, 1383.
(16) Collman, J. P.; Barnes, C. E.; Swepton, P. N.; Ibers, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 3500. Collman, J. P.; Barnes, C. E.; Collins, T. J.; Brothers, P. J.; Gallucci, J.; Ibers, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 7030.

0020-1669/85/1324-2857$01.50/0

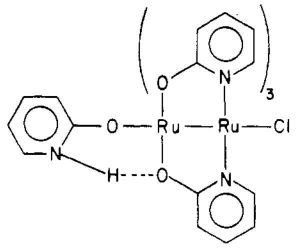
been reported, but they are generally less stable. Though +2 and +3 are considered[19] as stable oxidation states for individual ruthenium atoms, in diruthenium species the reason for the persistent stability of the Ru(II)Ru(III) unit, having the ground electronic configuration $(\sigma)^2(\pi)^4(\delta)^2(\pi^*)^2(\delta^*)^1$, with three unpaired spins occupying three nearly degenerate π^* and δ^* orbitals,[20] is still not clear.

Dimetal units with strong bonds can be stabilized by a number of bridging, three-atom ligands besides carboxyl groups,[1] but until recently the chemistry of diruthenium(II,III) had been restricted to the carboxylates. Recently, in this laboratory we have isolated[12,13] three new diruthenium(II,III) species using ligands of type **1**, namely, $Ru_2Cl(hp)_4(Hhp)$ (**2**), $Ru_2Cl(chp)_4$ (**3**), and $Ru_2Cl(PhNPy)_4$ (**4**). The arrangement of ligands in **2**–**4** is polar in nature. In **3** and **4** the torsion angle N–Ru–Ru–X is relatively large because of steric crowding of the four bulky groups on the same end. In the known[1] complexes of these ligands, the most common arrangement of ligands is of a 2:2 type. In some dirhodium complexes of chp and mhp, a 3:1 arrangement is known to occur.[21,22] In all cases, the formation of the unusual, completely polar arrangement is related to the strong axial coordination.[12,13,21-24] We were curious to see what would happen if we were to use mhp instead of chp as a bridging ligand. The van der Waals radius of CH_3 is larger than that of Cl, and the formation of $Ru_2Cl(mph)_4$ might thus require very large distortions of the ligands.



X	Y	Z	
O	H	H	Hhp
O	H	Cl	Hchp
O	H	CH_3	Hmhp
N	Ph	H	PhNHpy

1



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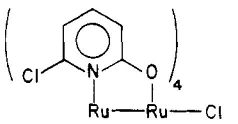

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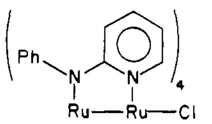

4

Reaction of $Ru_2Cl(O_2CCH_3)_4$ with a molten ligand such as Hchp was previously[12,13] proved to be an effective preparative method, but when this was tried with Hmhp, no clean product was obtained. It may be noted that the preparation and structure of $Ru_2(mhp)_4 \cdot CH_2Cl_2$ have been reported.[14,15] The preparation was achieved by reacting $Ru_2Cl(O_2CCH_3)_4$ with Na(mhp) in CH_3OH at room temperature, but the reported yield was only 8%. We have examined this type of reaction and by changing from Na(mhp) to Hmhp have been successful in isolating a crystalline product in almost quantitative yield. Elemental analysis and X-ray structural studies have shown it to be a mixed-ligand complex, $Ru_2Cl(O_2CCH_3)_2(mhp)_2 \cdot 0.5CH_2Cl_2$, the first of its kind in diruthenium chemistry. We report, in this paper, the synthesis, structure, and properties of this complex.

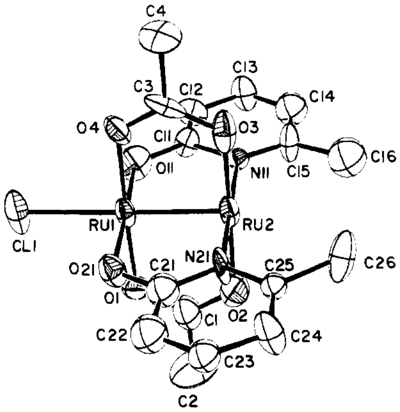

Figure 1. ORTEP diagram of the diruthenium complex in $Ru_2Cl(O_2CCH_3)_2(mhp)_2 \cdot 0.5CH_2Cl_2$ (**5**). Atoms are represented by thermal vibration ellipsoids at the 50% level and the atom-labeling scheme in this molecule is defined.

Experimental Section

Materials. $Ru_2Cl(O_2CCH_3)_4$ was prepared by following a literature method.[2] 6-Methyl-2-hydroxypyridine (Hmhp) was purchased from Aldrich Chemical Co. The solvents used in the electrochemical measurements were freshly distilled under dinitrogen. Tetrabutylammonium tetrafluoroborate ($(TBA)BF_4$) was used as a supporting electrolyte.

Preparation of $Ru_2Cl(O_2CCH_3)_2(mhp)_2 \cdot 0.5CH_2Cl_2$ (5). A mixture of 0.12 g (ca. 0.25 mmol) of $Ru_2Cl(O_2CCH_3)_4$ and 0.11 g (ca. 1.0 mmol) of Hmhp in 20 mL of CH_3OH was heated to reflux for 24 h. The color of the resulting solution was purple. After the methanol solvent was removed, the purple residue was dissolved in 20 mL of CH_2Cl_2. The solution was filtered, a 5-mL portion of the filtrate was placed in a test tube, and very carefully, a 10-mL layer of a 1:1 v/v mixture of pentane–diethyl ether was placed on the top of the CH_2Cl_2 solution. Slow diffusion of solvents gave very dark-colored crystals in *ca.* 80% yield. Anal. Calcd for $Ru_2Cl(O_2CCH_3)_2(mhp)_2 \cdot 0.5CH_2Cl_2$: C, 32.23; H, 3.09; N, 4.56. Found: C, 32.32; H, 3.16; N, 4.37. Infrared spectrum (KBr phase): 3030 (w), 1600 (w), 1545 (m), 1485 (m), 1448 (s), 1440 (s), 1405 (m), 1370 (m), 1345 (s), 1265 (w), 1250 (w), 1225 (w), 1162 (s), 1085 (w), 1035 (m), 1020 (s), 945 (m), 888 (w), 798 (s), 758 (s), 735 (m), 690 (s), 630 (s), 600 (w), 590 (m), 555 (w), 395 (s), 350 (s), 325 (w), 260 (w) cm^{-1} (m, medium; s, strong; w, weak). Electronic spectrum (CH_2Cl_2 solvent): λ_{max}, 550 nm (ϵ = 3370 M^{-1} cm^{-1}), 460 (sh), 378 (1540), 315 (sh), 292 (8070). The compound is soluble in CH_2Cl_2, $CHCl_3$, CH_3CN, acetone, and alcohols, slightly soluble in diethyl ether, and insoluble in pentane, hexane, and water.

Measurements. The elemental analysis was obtained from Galbraith Laboratories, Inc. The infrared and electronic spectra were recorded with Perkin-Elmer 785 and Cary 17D spectrophotometers, respectively. Electrochemical measurements were done, under argon atmosphere, with a Bioanalytical Systems, Inc., Model BAS 100 Electrochemical Analyser instrument in connection with a Bausch and Lomb, Houston Instruments Model DMP 40 digital plotter. In a three-electrode cell system, a Model BAS MF 2032 platinum disk and a platinum wire were used as working and auxiliary electrodes and a BAS MAF 2020 Ag–AgCl electrode was used as a reference electrode. All potentials were referenced to the Ag–AgCl electrode at 22 ± 2 °C and are uncorrected for junction potentials.

X-ray Crystallographic Procedures. The structure of the single crystal of $Ru_2Cl(O_2CCH_3)_2(mhp)_2 \cdot 0.5CH_2Cl_2$ was determined by using procedures documented elsewhere.[25] The compound crystallizes in the monoclinic space group $P2_1/c$ with four molecules per unit cell. Measurement of the unit cell constants and the data collection were done by using the Enraf-Nonius CAD-4 diffractometer and employing graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation. There was no decay of the crystal during 47 h of exposure time. The ruthenium atom positions were obtained from a three-dimensional Patterson map.[26]

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(17) Warren, L. F.; Goedken, V. L. *J. Chem. Soc., Chem. Commun.* **1978**, 909.

(18) Tooze, R. P.; Motevalli, M.; Hursthouse, M. B.; Wilkinson, G. *J. Chem. Soc., Chem. Commun.* **1984**, 799.

(19) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980.

(20) Norman, J. G.; Renzoni, G. E.; Case, D. A. *J. Am. Chem. Soc.* **1979**, *101*, 5256.

(21) Cotton, F. A.; Felthouse, T. R. *Inorg. Chem.* **1980**, *19*, 320.

(22) Berry, M.; Garner, C. D.; Hillier, I. H.; Clegg, W. *Inorg. Chim. Acta* **1980**, *45*, L209.

(23) Cotton, F. A.; Falvello, L. R.; Han, S.; Wang, W. *Inorg. Chem.* **1983**, *22*, 4106.

(24) Cotton, F. A.; Han, S.; Wang, W. *Inorg. Chem.* **1984**, *23*, 4762.

(25) Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 3358. Cotton, F. A.; Frenz, B. A.; Deganello, G.; Shaver, A. *J. Organomet. Chem.* **1973**, *50*, 227. North, A. C. T.; Phillips, D. C.; Mathews, F. A. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 351.

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

Table I. Crystallographic Data

formula	$Ru_2Cl(O_2CCH_3)_2(mhp)_2{\cdot}0.5CH_2Cl_2$ (**1**)
fw	614.36
space group	$P2_1/c$ (No. 14)
syst absences	$0k0$, $k = 2n$; $00l$, $l = 2n$; $h0l$, $l = 2n$
a, Å	8.508 (3)
b, Å	15.687 (7)
c, Å	15.759 (4)
α, deg	90.0
β, deg	93.49 (3)
γ, deg	90.0
V, Å^3	2099.3 (2)
Z	4
d_{calcd}, g/cm^3	2.079
cryst size, mm	0.2 × 0.2 × 0.1
μ(Mo Kα), cm^{-1}	18.36
data colln instrum	Enraf Nonius CAD-4
radiation (monochromated in incident beam)	Mo (Kα = 0.71073 Å)
orientation reflcns: no.; range (2θ), deg	25; $8 < 2\theta < 30$
temp, °C	25
scan method	ω–2θ
data colln range (2θ), deg	$5 \leq 2\theta \leq 50$
no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	3687, 1365
no. of params refined	209
transmission factors: max, min	99.86%, 92.19%
R^a	0.060
$R_w^{\ b}$	0.073
quality-of-fit indicator^c	1.67
largest shift/esd, final cycle	0.29
largest peak, e/Å^3	1.04

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

Table II. Table of Positional Parameters and Their Estimated Standard Deviations for $Ru_2Cl(O_2CCH_3)_2(mhp)_2{\cdot}0.5CH_2Cl_2$ (**1**)[a]

atom	x	y	z	B, Å^2
Ru(1)	0.1120 (2)	0.1554 (1)	0.7715 (1)	2.43 (3)
Ru(2)	0.3608 (2)	0.1554 (1)	0.8339 (1)	2.47 (3)
Cl(1)	−0.1504 (6)	0.1542 (4)	0.7031 (4)	5.1 (1)
O(1)	0.029 (1)	0.161 (1)	0.8867 (8)	3.5 (3)
O(2)	0.267 (2)	0.163 (1)	0.9512 (9)	4.1 (3)
O(3)	0.450 (1)	0.150 (1)	0.7230 (9)	3.7 (3)
O(4)	0.209 (1)	0.152 (1)	0.6553 (9)	3.4 (3)
O(11)	0.102 (2)	0.029 (1)	0.776 (1)	4.7 (4)
O(21)	0.114 (2)	0.2838 (9)	0.770 (1)	3.2 (3)
N(11)	0.362 (2)	0.027 (1)	0.8381 (9)	1.9 (3)*
N(21)	0.369 (2)	0.284 (1)	0.827 (1)	3.6 (4)
C(1)	0.118 (2)	0.162 (2)	0.956 (2)	4.2 (5)
C(2)	0.058 (4)	0.173 (2)	1.042 (2)	7.5 (8)
C(3)	0.350 (2)	0.149 (1)	0.654 (1)	3.7 (4)
C(4)	0.426 (3)	0.146 (2)	0.564 (1)	4.3 (5)
C(11)	0.227 (3)	−0.017 (1)	0.804 (1)	3.0 (4)
C(12)	0.219 (3)	−0.107 (1)	0.810 (1)	3.1 (5)
C(13)	0.350 (2)	−0.153 (1)	0.841 (1)	3.7 (5)
C(14)	0.477 (3)	−0.108 (2)	0.873 (2)	4.7 (6)*
C(15)	0.481 (2)	−0.019 (1)	0.873 (1)	3.6 (5)
C(16)	0.631 (3)	0.032 (2)	0.903 (2)	6.1 (7)*
C(21)	0.240 (3)	0.326 (1)	0.800 (2)	3.8 (4)*
C(22)	0.234 (3)	0.419 (2)	0.790 (2)	4.6 (5)*
C(23)	0.362 (2)	0.460 (1)	0.821 (1)	3.1 (4)*
C(24)	0.493 (2)	0.419 (1)	0.854 (2)	3.9 (6)
C(25)	0.493 (2)	0.330 (1)	0.854 (1)	2.3 (4)*
C(26)	0.642 (3)	0.277 (1)	0.887 (2)	4.5 (6)
Cl(2)	0.971 (0)	0.416 (0)	0.957 (0)	7.3 (5)*
Cl(3)	0.891 (0)	0.459 (0)	0.959 (0)	8.6 (5)*
C(5)	1.000 (0)	0.500 (0)	1.041 (0)	8 (2)*

[a] Starred atoms were refined isotropically. [b] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Remaining non-hydrogen atoms were located and refined by using least-squares refinements and difference Fourier maps.[26] There was one complete molecule per asymmetric unit. Some of the atoms were refined isotropically because their thermal ellipsoids became nonpositive definite on refining anisotropically. At the end of the refinements a disordered CH_2Cl_2 molecule with net occupancy of 0.5 was located. The C and Cl atoms of CH_2Cl_2 were refined isotropically with a site occupancy factor of only 0.125; evidently further disordered orientations are present but not definable. In the last cycle of refinement, the C and Cl atoms of CH_2Cl_2 were kept in the structure factor calculations but not in the least-squares refinement. The presence of half of the CH_2Cl_2 molecule per asymmetric unit was also evidenced from the elemental analysis. In the final cycle, 1365 unique data with $I > 3\sigma(I)$ were used to refine 209 parameters to final values of $R = 0.060$ and $R_w = 0.073$. The unusually low fraction of data (ca. 37%) with intensities $>3\sigma$ was of concern to us, but we cannot find any unique reason for this, other than some contribution from the disorder in the CH_2Cl_2 molecule. The failure of several atoms to refine anisotropically is also puzzling, but otherwise the structure refined well and shows no chemically or crystallographically suspicious features. Crystallographic data are summarized in Table I.

Results

Molecular Structure. The atomic positional parameters for $Ru_2Cl(O_2CCH_3)_2(mhp)_2{\cdot}0.5CH_2Cl_2$ are listed in Table II. The structure is shown in Figure 1, which also defines the atom numbering scheme. Selected bond distances and angles are presented in Table III.

The compound crystallizes in the monoclinic space group $P2_1/c$ with four molecules per unit cell. The asymmetric unit contains one complete diruthenium molecule and half of the CH_2Cl_2 molecule. While no crystallographic symmetry is required, the complex molecule possesses C_{2v} symmetry, with the C_2 axis coinciding with the essentially linear (179.0 (2)°) Cl(1)–Ru(1)–Ru(2) group. A stereoscopic view of the unit cell available as supplementary material shows the packing of the discrete diruthenium species and the disordered CH_2Cl_2 molecules, which do not interact with the complex.

The effective C_{2v} symmetry of the complex requires not only that the Cl(1)–Ru(1)–Ru(2) chain be essentially linear (as it is) but also that the bridging ligands be essentially planar and aligned so that there is little or no twisting about the Ru–Ru axis away from an eclipsed conformation. This is indeed the case. The individual torsion angles are as follows: 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°. The mean torison angle, therefore, is only 1.3°.

The absence of any significant twist is consistent with the fact that there are no strong steric forces that would operate to induce a twist. The distance between the methyl carbon atoms of the mhp ligands is 3.852 Å, which is only slightly less than twice the conventional van der Waals radius of a methyl group (2.0 Å). This situation is to be compared with that in $Ru_2Cl(chp)_4$[13] where a mean torsion angle of 18.8° is found. Here there are four Cl atoms on one end of the molecule so that there are four contacts between adjacent groups, and these distances are only $2^{-1/2}$ as great as the trans distances, which make them about 2.7 Å. Thus, even though the Cl atom has a slightly smaller van der Waals radius (1.8 Å) than the methyl group, the contacts of ca. 2.7 Å that would occur in an undistorted $Ru_2Cl(chp)_4$ molecule are so much shorter than the sum of van der Waals radii (3.6 Å) that a sizeable twist is produced. In addition, the $Ru_2Cl(chp)_4$ molecule shows another distortion that helps to relieve the Cl···Cl repulsions, namely a lengthening of the Ru–N bonds, which have a mean distance of 2.085 [6] Å in $Ru_2Cl(chp)_4$ as compared to 2.02 [2] Å in the present case.

Once again, even though there are only two methyl groups, this molecule is of the type where one end is blocked so that no axial ligand has access to Ru(2). It is therefore impossible to have infinite chains of the Ru_2···Cl···Ru_2···Cl··· type, and the chlorine atom is coordinated only to one ruthenium atom. This again results in a short Ru–Cl distance, 2.419 (5) Å. Comparison of

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(27) Chakravarty, A. R.; Cotton, F. A.; Tocher, D. A. *Polyhedron* **1985**, *4*, 1097.

Table III. Selected Bond Distances (Å) and Angles (deg) in $Ru_2Cl(O_2CCH_3)_2(mhp)_2 \cdot 0.5CH_2Cl_2$

Bond Distances			
Ru(1)–Ru(2)	2.278 (2)	O(11)–C(11)	1.34 (2)
–Cl(1)	2.419 (5)	O(21)–C(21)	1.32 (2)
–O(1)	1.988 (11)	N(11)–C(11)	1.41 (2)
–O(4)	2.056 (12)	N(11)–C(15)	1.33 (2)
–O(11)	1.99 (2)	N(21)–C(21)	1.33 (2)
–O(21)	2.013 (14)	N(21)–C(25)	1.32 (2)
Ru(2)–O(2)	2.061 (13)	C(1)–C(2)	1.48 (3)
–O(3)	1.950 (13)	C(3)–C(4)	1.60 (2)
–N(11)	2.02 (2)	C(15)–C(16)	1.55 (3)
–N(21)	2.02 (2)	C(25)–C(26)	1.58 (3)
O(1)–C(1)	1.29 (2)	Cl(2)–C(5)	1.340, 1.873
O(2)–C(1)	1.28 (2)	Cl(3)–C(5)	1.131, 1.674
O(3)–C(3)	1.34 (2)		
O(4)–C(3)	1.20 (2)		

Bond Angles			
Ru(2)–Ru(1)–Cl(1)	179.0 (2)	O(3)–Ru(2)–N(11)	89.3 (6)
–O(1)	88.7 (3)	–N(21)	88.8 (7)
–O(4)	88.3 (3)	Ru(1)–O(1)–C(1)	124 (1)
–O(11)	91.5 (5)	–O(4)–C(3)	118 (1)
–O(21)	89.8 (4)	–O(11)–C(11)	120 (1)
Ru(1)–Ru(2)–O(2)	89.3 (3)	–O(21)–C(21)	120 (1)
–O(3)	91.0 (3)	R(2)–O(2)–C(1)	120 (1)
–N(11)	90.9 (4)	–O(3)–C(3)	117 (1)
–N(21)	90.7 (5)	–N(11)–C(11)	118 (1)
Cl(1)–Ru(1)–O(1)	92.2 (4)	–C(15)	123 (1)
–O(4)	90.7 (4)	–N(21)–C(21)	119 (1)
–O(11)	88.1 (5)	–C(25)	124 (1)
–O(21)	90.6 (4)	O(1)–C(1)–O(2)	119 (2)
O(1)–Ru(1)–O(4)	176.9 (5)	O(3)–C(3)–O(4)	125 (2)
–O(11)	89.5 (7)	O(11)–C(11)–N(11)	119 (1)
–O(21)	88.3 (6)	O(21)–C(21)–N(21)	120 (2)
O(4)–Ru(1)–O(11)	91.4 (6)	Cl(2)–C(5)–Cl(3)	119.27
–O(21)	90.9 (6)		
O(11)–Ru(1)–O(21)	177.4 (5)		
O(2)–Ru(2)–O(3)	179.2 (7)		
O(2)–Ru(2)–N(11)	91.5 (6)		
–N(21)	90.7 (5)		

this distance with Ru–Cl distances in all other molecules where one or two chlorine atoms are the axial ligands can be made by consulting Table IV, which will be discussed further later on.

Electronic Spectrum. The electronic absorption spectrum of $Ru_2Cl(O_2CCH_3)_2(mhp)_2$ in CH_2Cl_2 solution is shown in Figure 2. The intense violet color of the compound is understandable in terms of this spectrum, which features a strong broad band centered at 550 nm (ϵ = 3370 M^{-1} cm^{-1}) with a shoulder at about 460 nm. There is a weak but resolved band at 378 nm (ϵ = 1540 M^{-1} cm^{-1}) and a strong band at 292 nm (ϵ = 8070 M^{-1} cm^{-1}). All compounds containing the Ru_2^{5+} unit bridged by four bidentate ligands and axially coordinated by chloride ions have a moderately strong absorption band in, or toward, the blue end of the visible spectrum. In $Ru_2Cl(O_2CR)_4$ compounds the band is at ca. 430 nm usually with an intensity of $\geq$1000 M^{-1} cm^{-1}, and in compounds **2**–**4** (cited in the introduction) the bands are found at 480 nm (ϵ = 4690 M^{-1} cm^{-1}), 536 nm (ϵ = 4740 M^{-1} cm^{-1}), and 764 nm (ϵ = 6910 M^{-1} cm^{-1}), respectively. Only for the tetracarboxylato case has there been discussion of the assignment,[6] and the matter is not conclusively settled. The nature of this band is probably basically the same in all cases, even though its position in $Ru_2Cl(O_2CCH_3)_2(mhp)_2$ (550 nm) is not between those for the bands in $Ru_2Cl(O_2CCH_3)_4$ (ca. 430 nm) and $Ru_2Cl(chp)_4$ (536 nm).

Electrochemistry. The redox chemistry of $Ru_2Cl(O_2CCH_3)_2(mhp)_2$ was studied in CH_2Cl_2 and CH_3CN solutions by cyclic and differential-pulse voltammetry. In CH_2Cl_2, the compound exhibits one reduction at –0.1 V and one oxidation at +1.64 V vs. Ag–AgCl reference electrode. The peak-to-peak separations, $\Delta E_p = E_{p,a} - E_{p,c}$, which lie between 60–65 mV, indicate the quasi-reversible nature of the processes. Controlled-potential coulometry done at potentials of –0.3 and +1.8 V shows these processes to be a one-electron reduction and a one-electron oxidation, respectively (eq 1). Cyclic voltammograms

$$\mathrm{Ru_2Cl(O_2CCH_3)_2(mhp)_2^+} \underset{\substack{-e^- \\ E_{1/2} = +1.64\ \mathrm{V} \\ (\Delta E_p = 65\ \mathrm{mV})}}{\overset{+e^-}{\rightleftharpoons}} \mathrm{Ru_2Cl(O_2CCH_3)_2(mhp)_2} \underset{\substack{-e^- \\ E_{1/2} = -0.10\ \mathrm{V} \\ (\Delta E_p = 62\ \mathrm{mV})}}{\overset{+e^-}{\rightleftharpoons}} \mathrm{Ru_2Cl(O_2CCH_3)_2(mhp)_2^-} \quad (1)$$

showing the reversible one-electron processes are presented in Figure 3. In acetonitrile solvent, the oxidation was observed at +1.47 V (ΔE_p = 70 mV) and two reductions take place at –0.12 V (ΔE_p = 70 mV) and +0.12 V (ΔE_p = 65 V) at 100 mV s^{-1}. The reduction peak at +0.12 V is less prominent, and this could be due to the couple between $Ru_2(O_2CCH_3)_2(mhp)_2^+$ and $Ru_2(O_2CCH_3)_2(mhp)_2$. In polar solvents, diruthenium(II,III) amidato and carboxylato complexes are known to undergo partial dissociation: [Ru–Ru–Cl] = $[Ru–Ru]^+ + Cl^-$.

Earlier electrochemical studies on $Ru_2Cl(O_2CR)_4$ and $Ru_2Cl(RCONH)_4$ compounds have shown that the redox processes observed at moderate potentials are metal centered.[8-11] We have recently reported data[28] for compounds **2**–**4**. The metal-centered oxidations in these compounds are found in the range +0.5 V to +1.2 V and the reductions in the range +0.1 V to –0.75 V. In general the redox properties of all diruthenium(II,III) compounds are similar, although the Ru_2^{5+} unit is better stabilized in $Ru_2Cl(O_2CCH_3)_2(mhp)_2$ than in the other complexes.

Discussion

We shall wish to compare the compound reported here with others containing the Ru_2^{5+} core. To facilitate this, and also to provide an overview of the rapid development that has occurred recently in this field, we have listed in Table IV all of the 13 compounds with Ru_2^{5+} cores whose structures are now known by X-ray crystallography. About half of these have been reported only within the last few years.

When the Ru_2^{5+} unit is coordinated by four uninegative, bridging bidentate ligands, there is still one uncompensated positive charge. This unit, therefore, has a marked attraction for axial ligands, especially those that are negatively charged. Thus, so long as the axial positions are not blocked, coordination occurs at both of them and we obtain compounds such as nos. 1 and 2 and Nos. 6-13 in Table IV. When the bridging ligands are such as to block the axial region, which is the case for $PhNpy^-$, chp^- and mhp^-, an interesting problem arises. Normally, four such ligands orient themselves so that two of them put their bulky substituents (6-Cl in chp^-, 6-CH_3 in mhp^-, etc.) toward one end of the M_2 unit and two of them point the other way. However, when this happens, both ends are blocked and *no* axial bonds can be formed.

We have pointed out in an earlier report[13] that provided the bulky ligands are not too bulky, there is a way that they may be arranged so that at least one end of the Ru_2^{5+} unit is accessible to an axial ligand, and that is by having all four bridging ligands oriented in the same direction. The end that is now encumbered by four blocking groups is no worse off than if there were only two (blocking groups), since even two (and probably even one) of these suffice to make it inaccessible to an axial ligand. However, the other end is now completely unencumbered and can form a strong bond to an axial ligand. This is exactly the situation that was previously found to prevail in compound nos. 3 and 4 in Table IV.

In these two compounds we see two other consequences of this unidirectional, or completely polar, arrangement of the bridging ligands. Because an axial ligand is present at only one end, this leads to a stronger and shorter metal–ligand bond as compared to the cases where there is an axial ligand at each end. The Ru–Cl bond lengths in all cases where there is one such bond at each

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(28) Chakravarty, A. R.; Cotton, F. A.; Tocher, D. A.; Tocher, J. H. *Polyhedron*, in press.

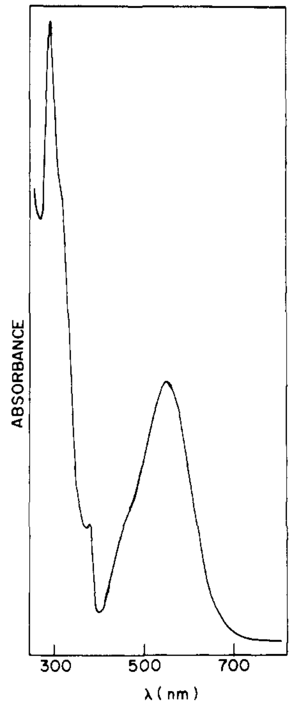

Figure 2. Electronic absorption spectrum of $Ru_2Cl(O_2CCH_3)_2(mhp)_2\cdot 0.5CH_2Cl_2$ in CH_2Cl_2.

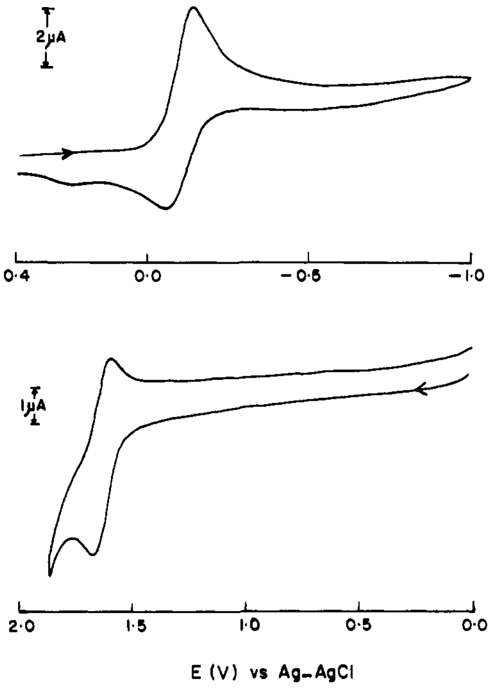

Figure 3. Cyclic voltammograms for $Ru_2Cl(O_2CCH_3)_2(mhp)_2\cdot 0.5CH_2Cl_2$ in CH_2Cl_2 at a scan rate of 100 mV s^{-1} in the presence of 0.1 M tetrabutylammonium tetrafluoroborate as a supporting electrolyte.

end are in the range between 2.517 (2) Å (no. 11) and 2.587 (5) Å (no. 6). Compound no. 8 also has a long Ru–Cl bond, 2.558 (2) Å, even though there is a Cl atom at only one end. However, in this case there is an Hhp molecule coordinated through its nitrogen atom at the other end. In the three compounds (including the present one) that have a Cl^- ligand at one end and no axial ligand at the other (nos. 3–5) the Ru–Cl distances are much shorter, namely, 2.419 (5), 2.437 (7), 2.443 (2) Å.

It is important to recognize, as we have already done,[13] that the placement of *four* blocking substituents at one end is not possible without strain and that this strain leads to a twisting of the bridging ligands so as to increase the distances between the substituents in adjacent ligands. In the case of $Ru_2Cl(PhNpy)_4$ this leads to a mean torsion angle about the Ru–Ru bond of 22.7° while in $Ru_2Cl(chp)_4$ the torsion angle is 18.8°. When there are only two blocking substituents trans to each other, there is much less repulsion since the distance between these two is $2^{-1/2}$ times as great as the four distances between adjacent substituents in the completely polar structure.

Table IV. Comparison of the Ru–Ru and Ru–Cl Distances in Diruthenium(II,III) Complexes

no.	compd	Ru–Ru, Å	Ru–Cl, Å	ref
1	$[Ru_2(OH_2)_2(O_2CCH_3)_4]BF_4$	2.248 (1)		4
2	$Ru_2Cl(O_2CCH_3)_4\cdot 2H_2O^a$	2.267 (1)	2.556 (1)	4
3	$Ru_2Cl(PhNpy)_4$	2.275 (3)	2.437 (7)	12
4	$Ru_2Cl(O_2CCH_3)_2(mhp)_2\cdot 0.5CH_2Cl_2$	2.278 (2)	2.419 (5)	this work
5	$Ru_2Cl(chp)_4\cdot CH_2Cl_2$	2.281 (1)	2.443 (2)	13
6	$Ru_2Cl(O_2CC_3H_7)_4{}^b$	2.281 (4)	2.587 (5)	3
7	$Ru_2Cl(O_2CCH_3)_4{}^b$	2.281 (3)	2.571 (4)	5b
8	$Ru_2Cl(hp)_4(Hhp)$	2.286 (1)	2.558 (2)	12
9	$Cs[Ru_2Cl_2(O_2CCH_3)_4]$	2.286 (2)	2.521 (4)	4
10	$Ru_2Cl(O_2CCH_3)_4$	2.287 (2)	2.577 (1)	6
11	$K[Ru_2Cl_2(O_2CH)_4]$	2.290 (1)	2.517 (2)	4
12	$Ru_2Cl(O_2CC_2H_5)_4$	2.292 (7)	2.566 (4)	4
13	$Ru_2Cl(4\text{-}Cl\text{-}C_6H_4CONH)_4\cdot CH_3OH^b$	2.296 [1]	2.583 [2]	27

[a] Polymeric species having linear Ru–Cl–Ru chains. [b] Polymeric species having zigzag Ru–Cl–Ru chains.

In preparing and characterizing the compound reported here, we were motivated by the question of how far the completely polar type of structure could continue to be tolerable as the steric bulk of the substituents continued to increase. Since the methyl group has a conventional van der Waals radius of 2.0 Å as compared to a radius of 1.8 Å for Cl, we wished to see whether one could still obtain a completely polar structure with mhp^-, that is, whether one could prepare the compound $Ru_2Cl(mhp)_4$. We have not been able to do this (which does not, of course, prove that it is impossible), but we have obtained instead a result that is quite logical and is consistent with our previous reasoning.

In the attempt to replace all four $CH_3CO_2^-$ ligands by mhp^- ligands, only two of them, trans to each other, were actually replaced and the two mhp^- ligands are oriented in the same direction. This blocks one end but leaves the other one free to accept an axial Cl^- ligand, which forms a short bond, 2.419 (5) Å. Moreover, the distance between the trans methyl atoms is great enough, 3.85 Å, that no serious steric problem arises and the molecule does not undergo any significant twist. On the other hand, if there were four mhp ligands all pointing the same way, there would be four methyl contacts of ca. 2.7 Å prior to any twisting. It is doubtful if any amount of twisting that would be tolerable in other parts of the molecule could relieve this.

An examination of the data listed in Table IV prompts one other observation. The compounds are listed there in order of increasing Ru–Ru bond length. It is evident that the entire range, 2.248 (1)–2.296 [1] Å, is not very large. Indeed, if we omit the one compound that does not have any axial anionic ligand (Cl^-), namely $[Ru_2(O_2CCH_3)_4(H_2O)_2](BF_4)$, the range is very narrow indeed, covering only 0.029 Å. It is interesting that there is no correlation between the Ru–Ru bond lengths and the Ru–Cl bond lengths. Thus, even though axial ligation seems to be important in these compounds, and intrinsically unfavorable arrangements of the bridging ligands are adopted to allow for at least one axial ligand, the Ru–Ru bond per se does not seem sensitive to the presence of these ligands.

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Registry No. 5, 96825-40-0; $Ru_2Cl_2(O_2CCH_3)_2(mhp)_2{}^+$, 96825-41-1; $Ru_2Cl_2(O_2CCH_3)_2(mhp)_2{}^-$, 96825-42-2; $Ru_2Cl(O_2CCH_3)_4$, 38833-34-0; Ru, 7440-18-8.

Supplementary Material Available: A stereoscopic view of the unit cell and tables of structure factors, anisotropic thermal parameters, and complete bond distances and angles (16 pages). Ordering information is given on any current masthead page.