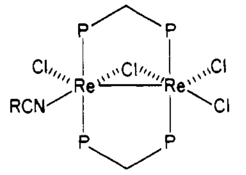
second stable intermediate (see the $^{31}P\{^1H\}$ NMR spectral results in Figure 4).

At the present time we are uncertain as to the structure of $Re_2Cl_4(dppm)_2(NCC_2H_5)$ since attempts to grow crystals of it in the absence of excess nitrile have been thwarted by its ready dissociative decomposition. One intriguing possibility is that it possesses the A-frame structure **1**, which is analogous to that which we have recently found is formed in the reaction of $Re_2Cl_4(dppm)_2$ with isocyanide ligands.[18] Indeed, certain dinuclear complexes that possess a trans dppm-bridged unit are known to undergo skeletal rearrangement via an A-frame type structure.[19] In support of structure **1**, we note that when an A-frame structure is present, the ^1H NMR spectrum of the methylene protons of the dppm ligands appears as a basic AB pattern with superimposed P–H coupling.[20-22] This is exactly what we observe in the spectrum of $Re_2Cl_4(dppm)_2(NCC_2H_5)$ (vide supra) and contrasts with the related NMR spectrum of $Re_2Cl_4(dppm)_2$ that shows[6] a pentet for the methylene resonance.



1

The formation of a bridged species such as **1** as a necessary prerequisite for these nitrile reactions to occur is also consistent with the fact that for $Re_2Cl_4(dppe)_2$ (dppe = 1,2-bis(diphenylphosphino)ethane) such a chlorine-bridged intermediate is unlikely to be accessible because of the bonding constraints imposed by the bridging dppe ligands.[23] In accord with this we find that $Re_2Cl_4(dppe)_2$ shows no tendency to react with nitriles under these same conditions.

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Supplementary Material Available: Full tables of anisotropic thermal parameters, bond distances, bond angles, and observed and calculated structure factors for the crystal structure of $[Re_2Cl_3(dppm)_2(NCC_6H_5)_2]PF_6$ (14 pages). Ordering information is given on any current masthead page.

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(18) The reaction of $Re_2Cl_4(dppm)_2$ with RNC gives the stable 1:1 adduct $Re_2Cl_4(dppm)_2(CNR)$. A single-crystal X-ray structure determination on the derivative where R = *t*-Bu has confirmed that this molecule has structure **1**, in which a multiply bonded dirhenium(II) unit is retained. A disorder problem is at present frustrating our attempts to refine the structure: Barder, T. J.; Powell, D.; Walton, R. A., unpublished results.

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New Isomeric Form of the "$M_2(OC_5H_3NCl)_4$" Core: A Polar Arrangement of the Four 6-Chloro-2-hydroxypyridinato (chp) Ligands in a Chlorodiruthenium(II,III) Complex, $Ru_2Cl(chp)_4$

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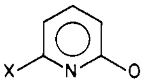
Received August 8, 1984

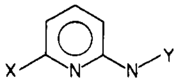
The compound $Ru_2Cl(chp)_4$ was prepared by reacting $Ru_2Cl(O_2CCH_3)_4$ with Hchp (6-chloro-2-hydroxypyridine) at 135 °C. Crystals of composition $Ru_2Cl(chp)_4{\cdot}CH_2Cl_2$ were obtained by slow diffusion of hexane into a CH_2Cl_2 solution of $Ru_2Cl(chp)_4$. The crystalline compound was characterized analytically and spectroscopically. The structure has been determined by X-ray crystallography. The crystals are orthorhombic and belong to the space group *Pbcn* with a = 15.645 (4) Å, b = 11.861 (3) Å, c = 16.942 (4) Å, V = 3144 (2) Å^3, and Z = 4. The compound has four bridging chp ligands that are oriented in one direction to form a polar molecule. In $Ru_2Cl(chp)_4{\cdot}CH_2Cl_2$, the ruthenium having one axial chlorine atom is bonded to four oxygen atoms. The other ruthenium is bonded to four nitrogen atoms. The molecule is twisted away from an eclipsed conformation by approximately 19°. The CH_2Cl_2 molecule is present as a solvent of crystallization and does not interact with the complex molecule. The Ru–Ru bond length is 2.281 (1) Å, and the metal–metal bond order is 2.5. The Ru–Cl, average Ru–O, and average Ru–N bond lengths are 2.443 (2), 2.002 [5], and 2.085 [6] Å, respectively. The purple solution of the compound in CH_2Cl_2 exhibits a band at 536 nm (ϵ = 4740 M^{-1} cm^{-1}) in the electronic spectrum.

Introduction



1

hp: X=H
mhp: X=CH_3
chp: X=Cl
fhp: X=F



2

ap: X=Y=H
map: X=CH_3, Y=H
PhNpy: X=H, Y=C_6H_5

Bridging ligands of the types **1** and **2** are known[1] to be good stabilizers of dimetal units with short metal–metal bonds. It has been found that the steric and electronic nature of the substituents X and Y play a critical role in dictating the geometry and the metal–metal bond length of a complex molecule. In complexes of the types $M_2(mhp)_4$[2,3] and $M_2(chp)_4$[3,4] (M = Cr, Mo, W, Rh), the disposition of the four bridging ligands about the dimetal unit is generally such that each metal is coordinated to two O atoms and two N atoms, thus giving what we call the 2:2 arrangement. A similar arrangement has also been observed[5] in the $M_2(PhNpy)_4$ complexes of molybdenum and tungsten. In some dirhodium species a 3:1 arrangement of ligands has been observed.[3,6] In

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these compounds one rhodium atom is coordinated by three nitrogen atoms and one oxygen atom while the other rhodium atom is bonded to three oxygen atoms and one nitrogen atom.

A completely polar arrangement of ligands (i.e., a 4:0 arrangement) was first observed[7,8] in the $M_2(fhp)_4(THF)$ (M = Cr, Mo, W, Rh) complexes in which one metal atom has only M–N bonds while the other has four M–O bonds. We recently reported[9] two polar diruthenium(II,III) complexes, viz. $Ru_2Cl(hp)_4(Hhp)$ and $Ru_2Cl(PhNpy)_4$. In the latter compound, the ruthenium atom having the axial chlorine atom is bonded to four pyridine nitrogen atoms while the other ruthenium atom is bonded to the four amine nitrogen atoms. The axial site on this ruthenium atom is blocked by the four pendant phenyl groups, thus giving a discrete molecule instead of a polymeric structure such as that found in $Ru_2Cl(O_2CR)_4$.[10] In the hp complex, the arrangement is also completely polar although there are no steric reasons other than the presence of an axial Hhp ligand hydrogen bonded to one bridging hp ligand. This may stabilize the polar arrangement over the usual 2:2 arrangement.

In this paper we report the synthesis, structure, and properties of a new compound, $Ru_2Cl(chp)_4\cdot CH_2Cl_2$, that constitutes the first example of a totally polar molecule having chp as the bridging ligands. The previously known[11] mhp complex of diruthenium(II,II), $Ru_2(mhp)_4\cdot CH_2Cl_2$, which has no axial ligands, has the usual 2:2 ligand array.

Experimental Section

Materials. $Ru_2Cl(O_2CCH_3)_4$ was prepared[12] by using a literature method. The ligand 6-chloro-2-hydroxypyridine (Hchp), purchased from Aldrich Chemical Co., was purified by sublimation prior to use.

Preparation of $Ru_2Cl(chp)_4\cdot CH_2Cl_2$. A mixture of 0.1 g of $Ru_2Cl(O_2CCH_3)_4$ and 1.0 g of Hchp was heated at 135 °C for 48 h under a dinitrogen atmosphere. Excess ligand was then sublimed off under vacuum at 135 °C, leaving a residue that was purple. A 0.5-g sample of the product was dissolved in 10 mL of CH_2Cl_2, and the solution was filtered. The purple solution was placed in a test tube, and, very carefully, 15 mL of hexane was layered on the top of this solution. Slow diffusion of hexane into the CH_2Cl_2 solution gave dark, large, single crystals in ca. 80% yield. Anal. Calcd for $Ru_2Cl_7N_4O_4C_{21}H_{14}$: C, 30.12; H, 1.67; N, 6.69. Found: C, 29.87; H, 1.97; N, 6.23. The compound is soluble in CH_2Cl_2, CH_3CN, acetone, and alcohols, slightly soluble in diethyl ether, and insoluble in hexane and water. Infrared spectrum (KBr phase): 3080 (w), 3060 (w), 1588 (s), 1525 (s), 1435 (s), 1425 (s), 1380 (m), 1340 (s), 1258 (w), 1170 (s), 1075 (w), 1012 (s), 925 (s, br), 790 (s), 720 (s), 695 (w), 628 (s) 610 (w), 600 (w), 445 (w), 390 (w), 365 (m), 340 (w), 310 (w), 280 (w), 255 (w) cm^{-1} (key: br, broad; m, medium; s, strong; w, weak). Electronic spectrum (820–320 nm, CH_2Cl_2 solvent): λ_{max} 680 nm (br, ϵ = 980 M^{-1} cm^{-1}), 536 (4740), 440 (sh), 380 (sh), 340 (sh).

Measurements. The elemental analysis was obtained from Galbraith Laboratories, Inc. The infrared and electronic spectra were recorded on Perkin-Elmer 785 and Cary 17D spectrophotometers, respectively.

X-ray Crystallographic Procedures. The structure of the single crystal of $Ru_2Cl(chp)_4\cdot CH_2Cl_2$ was determined by using the general procedures described elsewhere.[13,14] A detailed description is available as supplementary material. Pertinent crystallographic data are summarized in Table I. Complete tables of bond distances and angles along with anisotropic thermal parameters and structure factors are available as supplementary material. A brief description of the structure determination is presented below.

Table I. Crystallographic Data

formula	$Ru_2Cl(C_5H_3NOCl)_4\cdot CH_2Cl_2$ (1)
fw	836.68
space gp	*Pcbn*
syst abs	$0kl$ ($k = 2n$), $h0l$ ($l = 2n$), $hk0$ ($h + k = 2n$), $h00$ ($h = 2n$), $0k0$ ($k = 2n$), $00l$ ($l = 2n$)
a, Å	15.645 (4)
b, Å	11.861 (3)
c, Å	16.942 (4)
α, deg	90.0
β, deg	90.0
γ, deg	90.0
V, Å³	3144 (2)
Z	4
d_{calcd}, g/cm³	1.768
cryst size, mm	0.5 × 0.5 × 0.3
μ(Mo Kα), cm⁻¹	15.76
data colln instrum	Nicolet P3
radiation (monochromated in incident beam	Mo Kα (λ = 0.71073 Å)
orientation reflcns: no.; range (2θ)	25; 21° < 2θ < 30°
temp, °C	25 ± 1
scan method	ω-2θ
data colln range (2θ), deg	5-50
no. of unique data; total with $F_o^2 > 3\sigma(F_o^2)$	1659; 1491
no. of parameters refined	187
transmissn factors: max, min	99.19, 75.15
R^a	0.038
R_w^b	0.060
quality-of-fit indicator^c	1.37
largest shift/esd, final cycle	0.65
largest peak, e/Å³	0.75

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

A dark single crystal of size 0.5 × 0.5 × 0.3 mm was wedged in a glass capillary with its mother liquor to avoid loss of the solvent of crystallization. Measurement of the unit cell constants and data collection were done on a Nicolet P3 autodiffractometer equipped with graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation. Lorentz, polarization, and absorption corrections were applied to the data. The space group *Pbcn* was determined by observing the systematic absences in the data set. The Ru atom positions were obtained from the direct-methods program MULTAN82. The remaining non-hydrogen atoms were found from least-squares refinements and difference Fourier maps. The two ruthenium atoms and the chlorine atom axially bonded to one ruthenium atom are on special positions, along a C_2 axis. The CH_2Cl_2 molecules of crystallization, which half-occupy a set of general positions near the C_2 axis, do not interact with the complex molecule. The unit cell packing diagram is available in the supplementary material. Only half of the complex molecule and half of the solvent molecule constitute the asymmetric unit. All the atoms were refined anisotropically. In the final cycle, 1491 unique data with $I > 3\sigma(I)$ were used to refine 187 parameters to final values of $R = 0.038$ and $R_w = 0.060$. The final difference Fourier map is featureless and had the highest peak with 0.75 e/Å³.

Results and Discussion

Preparation. The compound was prepared by reacting $Ru_2Cl(O_2CCH_3)_4$ with molten Hchp. This reaction route has been previously employed[9,15,16] in the synthesis of some other diruthenium compounds having three-atom-bridging ligands. As in the other cases, this method again afforded an almost quantitative yield of the product. It is known[15,16] that the reaction between $Ru_2Cl(O_2CCH_3)_4$ and acid amides of the type $RCONH_2$, where R = CF_3 or Ph, forms polymeric compounds like the starting

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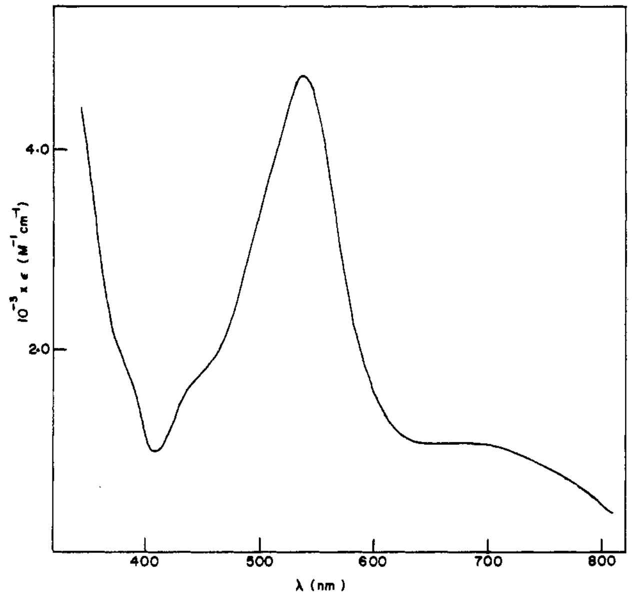

Figure 1. Electronic spectrum of $Ru_2Cl(chp)_4{\cdot}CH_2Cl_2$ in CH_2Cl_2.

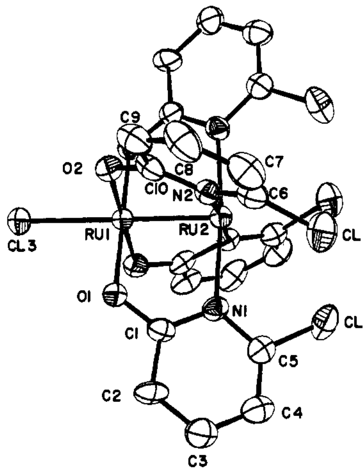

Figure 2. ORTEP diagram of the $Ru_2Cl(chp)_4$ molecule. Atoms are represented by thermal vibration ellipsoids at the 50% level, and the atomic labeling scheme in this molecule is defined.

carboxylates; however, similar reaction with ligands of type **1** or **2** gives discrete molecular species. Although the mean metal oxidation states remain unchanged during the course of the reaction, the steric constraints imposed on substitution of $RCOO^-$ dictate the geometry of the complex; e.g., $Ru_2Cl(hp)_4(Hhp)$ has two axial ligands while $Ru_2Cl(PhNpy)_4$ and $Ru_2Cl(chp)_4$ have only one axially coordinated ligand.

The electronic spectrum of $Ru_2Cl(chp)_4$ in CH_2Cl_2, as shown in Figure 1, exhibits a sharp band at 536 nm ($\epsilon = 4740$ M^{-1} cm^{-1}) with three shoulders at 440, 380, and 340 nm. There is also a broad band at 680 nm. The low-energy absorption bands observed[9] in $Ru_2Cl(hp)_4(Hhp)$ and $Ru_2Cl(PhNpy)_4$ are at 480 nm ($\epsilon = 4690$ M^{-1} cm^{-1}) and 764 nm ($\epsilon = 6910$ M^{-1} cm^{-1}), respectively. The similarity of the molar extinction coefficients in all three complexes suggests that the transitions may be of similar origin. A considerable shift is observed on going from hp to chp to PhNpy complexes.

Molecular Structure. The positional parameters for $Ru_2Cl(chp)_4{\cdot}CH_2Cl_2$ are given in Table II. Selected bond distances and angles are presented in Table III. Figure 2 is an ORTEP diagram of the complex molecule with the atom-labeling scheme shown.

The molecule consists of a diruthenium unit having four bridging chp ligands and one axial chloride ligand. The four chp ligands all point the same way so that one metal atom is coordinated entirely by nitrogen atoms and the other entirely by oxygen atoms. The axial chloride ligand is attached to the metal atom that is bound to the oxygen atoms of the chp ligands. The two ruthenium atoms and the axial chlorine atom, Cl(3), lie on a crystallographic twofold axis parallel to the *y* direction. Thus, the entire molecule has rigorous C_2 symmetry. Because of twisting of the chp ligands about this axis, (vide infra) C_4 is, in fact, the highest effective symmetry that can be ascribed to the molecule.

The twisting of the molecule is quantified by the torsion angles listed in Table IV, and its effect on molecular shape can be appreciated by examination of Figure 3, a view down the Ru–Ru axis showing how the sets of four N atoms, four O atoms, and

Table II. Table of Positional Parameters and Their Estimated Standard Deviations for $Ru_2Cl(chp)_4{\cdot}CH_2Cl_2$ (**1**)

atom	*x*	*y*	*z*	*B*,[a] Å^2
Ru(1)	0.500	0.01216 (7)	0.250	2.22 (2)
Ru(2)	0.500	−0.18015 (6)	0.250	2.16 (2)
Cl(1)	0.6524 (2)	−0.3738 (2)	0.2825 (2)	4.39 (5)
Cl(2)	0.4702 (2)	−0.3808 (2)	0.3825 (1)	4.45 (5)
Cl(3)	0.500	0.2181 (2)	0.250	3.61 (6)
Cl(4)	0.7985 (3)	−0.2843 (3)	0.4999 (2)	9.2 (1)
Cl(5)	0.8331 (5)	−0.0897 (4)	0.4127 (4)	17.6 (2)
O(1)	0.6093 (3)	0.0123 (4)	0.1889 (3)	2.6 (1)
O(2)	0.5647 (3)	0.0110 (4)	0.3521 (3)	3.0 (1)
N(1)	0.6309 (4)	−0.1714 (5)	0.2242 (4)	2.6 (1)
N(2)	0.5274 (4)	−0.1750 (5)	0.3697 (4)	2.4 (1)
C(1)	0.6595 (5)	−0.0741 (6)	0.1925 (4)	2.7 (2)
C(2)	0.7449 (5)	−0.0616 (7)	0.1626 (5)	3.1 (2)
C(3)	0.8008 (5)	−0.1511 (7)	0.1725 (5)	3.9 (2)
C(4)	0.7717 (5)	−0.2505 (8)	0.2107 (5)	3.6 (2)
C(5)	0.6896 (5)	−0.2562 (7)	0.2339 (4)	2.9 (2)
C(6)	0.5186 (5)	−0.2628 (7)	0.4211 (5)	3.1 (2)
C(7)	0.5429 (7)	−0.2621 (8)	0.4990 (5)	4.2 (2)
C(8)	0.5794 (6)	−0.1614 (8)	0.5277 (5)	4.5 (2)
C(9)	0.5892 (6)	−0.0680 (8)	0.4789 (5)	3.7 (2)
C(10)	0.5606 (5)	−0.0763 (6)	0.3979 (5)	2.8 (2)
C(11)	0.830 (1)	−0.237 (1)	0.4105 (7)	9.6 (4)

[a] 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. Selected Bond Distances and Angles for $Ru_2Cl(chp)_4{\cdot}CH_2Cl_2$ (**1**)[a]

Bond Distances (Å)			
Ru(1)-Ru(2)	2.281 (1)	O(1)-C(1)	1.293 (8)
-Cl(3)	2.443 (2)	O(2)-C(10)	1.295 (8)
-O(1)	1.999 (4)	N(1)-C(1)	1.350 (8)
-O(2)	2.005 (5)	-C(5)	1.371 (9)
Ru(2)-N(1)	2.096 (5)	N(2)-C(6)	1.364 (9)
-N(2)	2.074 (6)	-C(10)	1.367 (8)
Cl(1)-C(5)	1.721 (8)	C(11)-Cl(4)	1.690 (11)
Cl(2)-C(6)	1.721 (8)	-Cl(5)	1.749 (13)

Bond Angles (deg)			
Ru(2)-Ru(1)-Cl(3)	180.00 (0)	N(1)-Ru(2)-N(1)	174.4 (3)
-O(1)	90.1 (1)	-N(2)	89.8 (2),
-O(2)	89.6 (1)		90.0 (2)
Cl(3)-Ru(1)-O(1)	89.9 (1)	N(2)-Ru(2)-N(2)	176.6 (3)
-O(2)	90.4 (1)	Ru(1)-O(1)-C(1)	119.6 (4)
O(1)-Ru(1)-O(2)	89.1 (2),	-O(2)-C(10)	119.8 (4)
	90.9 (2)	Ru(2)-N(1)-C(1)	116.7 (4)
-O(1)	180.00 (0)	-C(5)	126.4 (5)
O(2)-Ru(1)-O(2)	179.2 (3)	C(1)-N(1)-C(5)	116.9 (6)
Ru(1)-Ru(2)-N(1)	87.2 (2)	Ru(2)-N(2)-C(6)	125.5 (5)
-N(2)	88.3 (2)	-C(10)	116.4 (5)
		C(6)-N(2)-C(10)	118.0
		Cl(1)-C(5)-N(1)	115.2 (5)
		-C(4)	120.2 (6)
		Cl(2)-C(6)-N(2)	115.0 (5)
		-C(7)	119.4 (7)
		O(1)-C(1)-N(1)	119.8 (6)
		O(2)-C(10)-N(2)	119.7 (6)
		Cl(4)-C(11)-Cl(5)	108.7 (7)

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

Table IV. Comparison of the Torsional Angles in Polar Diruthenium Complexes

compd	atom 1	atom 2	atom 3	atom 4	angle, deg
$Ru_2Cl(chp)_4\cdot CH_2Cl_2$	O(1)	Ru(1)	Ru(2)	N(1)	19.2
	O(2)	Ru(1)	Ru(2)	N(2)	18.4
$Ru_2Cl(PhNpy)_4$ [a]	N(2)	Ru(1)	Ru(2)	N(1)	22.8
	N(4)	Ru(1)	Ru(2)	N(3)	22.6
$Ru_2Cl(hp)_4(Hhp)$ [b]	N(1)	Ru(1)	Ru(2)	O(1)	4.3
	N(2)	Ru(1)	Ru(2)	O(2)	7.3
	N(3)	Ru(1)	Ru(2)	O(3)	5.0
	N(4)	Ru(1)	Ru(2)	O(4)	3.4

[a] N(1), N(3) and N(2), N(4) are amine and pyridine nitrogens, respectively.[9] [b] Reference 9.

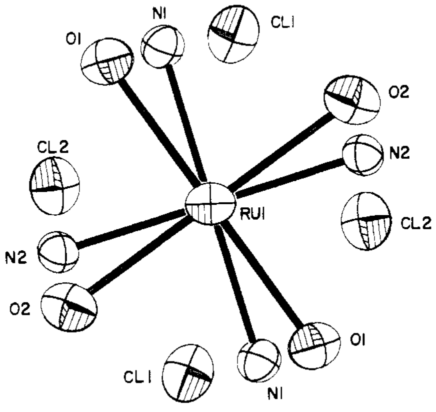

Figure 3. View down the Ru(1)–Ru(2) axis in the $Ru_2Cl(chp)_4$ molecule, showing the arrangement of the coordinated atoms and the chlorine atoms of the chp ligands.

four Cl atoms of the chp ligands are related to one another.

In an earlier paper[8] concerning the structure of $Rh_2(fhp)_4(Me_2SO)$, it was pointed out that the polar structure in that molecule, and in the $M_2(fhp)_4(THF)$ molecules (M = Cr, Mo, W) as well, might be attributed to the fact that the four fluorine atoms can be accommodated at one end of the M_2 unit without excessive crowding, thus leaving the other end free to form the best possible bond to an axial ligand. If a 2:2 arrangement of the fhp ligands were adopted, it might not be possible to form axial bonds at either end. It was further pointed out that for chp the larger chlorine atoms would encounter serious crowding in the polar arrangement and would, therefore, not be expected to adopt it. Indeed, for the $M_2(chp)_4$ (M = Cr, Mo, W) molecules a 2:2 arrangement has been found.[4]

The fact that we have found the completely polar arrangement in $Ru_2Cl(chp)_4$ does not stand in contradiction to the above arguments. Rather, it shows that still other factors must be considered in order to have a complete understanding of these structures. Two new factors come into play in this case: (1) We are now dealing with a dimetal unit, Ru_2^{5+}, that requires an additional anion, and this anion, Cl^-, has a tendency to form an axial bond to the $Ru_2(chp)_4^+$ cation. (2) The Ru_2^{5+} unit with its $\sigma^2\pi^4\delta^2\pi^{*2}\delta^*$ electronic configuration has only a small barrier to rotation.

While a strictly eclipsed $Ru_2(chp)_4^+$ unit would indeed, as noted earlier,[8] have unacceptably close chlorine atoms, by twisting of the chp ligands about the Ru–Ru bond, the Cl···Cl distance can be considerably increased so that at the torsion angles adopted here (mean value 18.8°) the Cl(1)···Cl(2) and Cl(1)···Cl(2)′ distances are 3.32 and 3.39 Å. These are still less than the van der Waals distance of 3.6 Å but are not unreasonable intramolecular contacts. For example, in all of the $[M_2Cl_8]^{n-}$ species, the Cl···Cl distances are in the range 3.20–3.45 Å. Thus, twisting can and does relieve the repulsive forces between the chp chlorine atoms enough so that the polar arrangement can form. It is unlikely that in the $[Ru_2(chp)_4]^+$ ion itself it would occur, but when the additional stabilization provided by the formation of the axial Ru–Cl bond comes into play, the observed $Ru_2Cl(chp)_4$ structure becomes the best one available.

The axial Ru–Cl bond length, 2.443 (2) Å, is much shorter than those in the polymeric $Ru_2(O_2CR)_4Cl$ compounds,[10] which are about 2.56 Å; it is also shorter than that in $Ru_2Cl(hp)_4(Hhp)$,[9] where the value is 2.558 (2) Å. In these cases, axial bonds are being formed at both Ru atoms and this presumably leads to each one being weaker and longer. In $Ru_2Cl(PhNpy)_4$, however, where the situation[9] is very similar to that found here, the one axial Ru–Cl bond is again short, 2.437 (7) Å.

The average Ru–O and Ru–N distances of 2.002 [5] and 2.085 [6] Å and the various mean angles, viz., Ru–Ru–O = 89.9 [1]°, Ru–Ru–N = 87.8 [2]°, O–Ru–O = 90.0 [2]°, and N–Ru–N = 89.9 [2]°, are all of reasonable and expected magnitudes.

General Comments. The present compound is another example of the formal Ru(II)–Ru(III) type in which there is a total of 11 electrons available to fill orbitals that play a role in metal–metal bonding. Although we have not made a magnetic measurement in this case, this molecule presumably has three unpaired electrons, like the others, and can be assigned an electron configuration $\sigma^2\pi^4\delta^2\pi^{*2}\delta^*$. The Ru–Ru bond length in this case, 2.281 (1) Å, is very similar to those in the $Ru_2Cl(hp)_4(Hhp)$ and $Ru_2Cl(PhNpy)_4$ molecules, which are 2.286 (1) and 2.275 (3) Å, respectively. For the latter two compounds, magnetic measurements were made and showed three unpaired electrons. The great similarity of the Ru–Ru distances in these three polar compounds despite some differences in the details of axial ligation and the magnitude of internal twist indicates that small variations in these latter features are not important in controlling the strength of the Ru–Ru bonding. This is somewhat in contrast to the behavior of quadruply bonded molybdenum systems where a clear dependence of Mo–Mo bond length on the twist angle has been found.[17]

The distance in $Ru_2Cl(chp)_4$ is about 0.04 Å longer than that in $Ru_2(mhp)_4$, where it is 2.238 (1) Å.[11] The two ligands, mhp^- and chp^-, are similar, but the complexes differ in many ways, any of which might influence the bond length. Rather than attempt any general discussion of the entire range of factors, let us simply deal with the one most obvious question: since the formal bond order (2.0) in $Ru_2(mhp)_4$ is lower than that (2.5) in $Ru_2Cl(chp)_4$, why is the bond shorter by 0.04 Å. Probably the two most important factors are the presence of an axial ligand in the latter compound and the higher formal charge on the metal atoms. The tendency of M–M multiple-bond distances to increase when axial ligands are appended is well-known. In addition, it has recently been shown in some detail[18-20] that an increase in the effective positive charges on the metal atoms can cause a reduction in the extent to which the σ and π, as well as the δ orbitals, overlap, thus weakening and lengthening M–M bonds by amounts comparable to, or greater than, the increases that might be expected from increases in bond orders by 0.5 or even 1.0 unit.

It may be noted that the Ru–Ru distances in the carboxylato-bridged II,III species,[1] $Ru_2Cl(O_2CR)_4$, are also close to 2.28 Å, whereas longer distances have recently been found both in a III,III compound, $Ru_2(CH_2CMe_3)_6$, 2.311 (3) Å,[21] and in a II,II compound, $Ru_2(OEP)_2$, 2.408 (1) Å.[22]

Concluding Remarks. We have seen from our studies that a preference for the polar or partially polar arrangement of ligands in Cr_2, Mo_2, W_2, Rh_2, and Ru_2 compounds, rather than the usual 2:2 arrangement, is strongly associated with the presence of strong axial coordination on one metal. Though the crowding of the bulky X or Y groups along one direction may, in itself, be an energetically unfavorable situation, the molecule is stabilized by the

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formation of a strong axial bond. In the present case the steric repulsion is also relieved by a considerable twisting (18.8°) of the bridging ligands. In $Ru_2(mhp)_4$[11] where there is no axial coordination, the molecule has a 2:2 arrangement, as expected.

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Supplementary Material Available: Details of the crystal structure determination, a unit cell diagram, and tables of structure factors, anisotropic thermal parameters, and bond distances and angles (16 pages). Ordering information is given on any current masthead page.

Notes

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Kinetics of the Reduction of Manganese(III) Porphyrins by Hexaammineruthenium(II): A Reductive Acid Solvolysis Mechanism

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The reagents ascorbic acid,[1] pentacyanocobaltate(II),[2] dithionite,[3-6] europium(II),[7] chromium(II),[7-11] tin(II),[12] and vanadium(II)[7,8] have been used to probe the mechanisms of reduction of trivalent iron, cobalt, and manganese water-soluble porphyrins to their divalent forms. In many cases, the reactions are of uncertain mechanism and with strong reductants and hydrodynamically easily reduced porphyrins, both central metal ion and ring reduction occur. The $Ru(NH_3)_6^{2+}$ ion is a well-characterized weak outer-sphere reductant, and its reactions with cobalt(III)[8,13,14] and iron(III)[15] porphyrins have been analyzed in terms of the Marcus theory[16] to provide electron-exchange rate constants for these coordinated metal ions. We report the reduction kinetics of several manganese(III) metalloporphyrins with $Ru(NH_3)_6^{2+}$. The overall mechanism involves a reductive demetalation process, and the results are compared with related electron-transfer and acid solvolysis reactions.

Experimental Section

Trifluoromethanesulfonic acid (3M Co.) was distilled under reduced pressure as the monohydrate (HTF). Lithium triflate was prepared from HTF and Li_2CO_3. Hexaammineruthenium(III) chloride (Matthey Bishop) was purified by recrystallization[17] and converted into the triflate salt[18] by precipitation of the chloride salt from distilled water using HTF. The sodium salt of manganese(III) tetrakis(4-sulfonatophenyl)porphyrin, Mn^{III}–TPPS, was prepared by literature methods.[19]

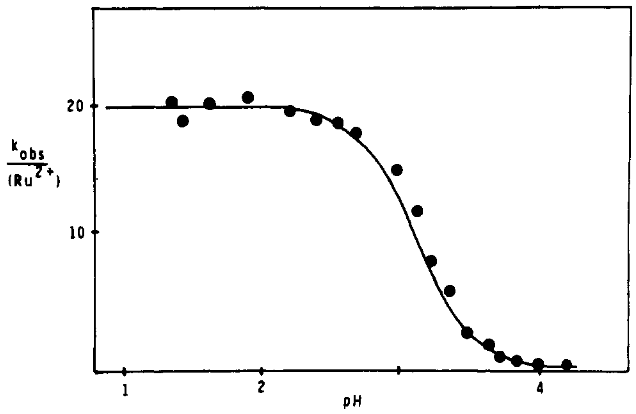

Figure 1. pH profile of the specific rates of the $Ru(NH_3)_6^{2+}$ reduction of Mn^{III}–TPPS at 25 °C and $I = 0.3$ (HTF/LiTF). The dots are experimental points, and the solid line is the theoretical curve calculated from eq 4.

All solutions were deaerated with chromous scrubbed argon. $Ru(NH_3)_6^{3+}$ was reduced to the divalent state with Zn-Hg and analyzed either by titration with permanganate[8] or spectrophotometrically by reduction of iron(III) and determination of the iron(II) formed as the tris(*o*-phenanthroline) complex.[17] The solutions were handled in Hamilton all-glass syringes with platinum needles, as stainless steel needles caused reduction of Mn^{III}–TPPS in acid.

The kinetics were followed at 25 °C on a Beckman Acta III recording spectrophotometer, or with a Durrum Gibson stopped-flow apparatus. The ionic strength (I) was maintained at 0.3 (HTF/LiTF). Chloroacetic acid (7.5×10^{-3} M) was the buffer between pH 2 and 4, while phthalic acid at the same concentration was used between pH 4 and 5. The reactions were run under pseudo-first-order conditions, with a greater than 100-fold excess of ruthenium to porphyrin (ca. 10^{-6} M). The reactions were found to be first order in Mn^{III}–P over 3 half-lives.

Results

At pH 1 ($I = 0.5$ (NaCl/HCl)), Mn^{III}–TPPS had bands at 466 nm ($\epsilon = 9.8 \times 10^4$ M^{-1} s^{-1}), 400 nm (6.1×10^4 M^{-1} s^{-1}), and 377 nm (5.9×10^4 M^{-1} s^{-1}). The compound followed Beer's law from 1×10^{-4} to 1×10^{-6} M at this pH, a result in agreement with relaxation studies[20] indicating that Mn^{III}–TPPS is monomeric in acid solution. The absorption spectra of constant concentrations of Mn^{III}–TPPS at the same ionic strength ($I = 0.2$) were carefully monitored between pH 1 and 10, and no changes were observed. Above pH 10, the Soret band decreased and broadened with further increases in pH. It appears that H_2O–Mn^{III}–TPPS does not hydrolyze below pH 10, while a variety of forms (HO–Mn^{III}–P, $(HO)_2$–Mn^{III}–P, and P–Mn^{III}–O–Mn^{III}–P) may occur in the basic region.

Between pH 1 and 4, the addition of excess $Ru(NH_3)_6^{2+}$ to Mn^{III}–TPPS produces sets of isosbestic points (the same as shown[12] in the Sn^{II}/Mn^{III}–TPPS reaction in 1 M HCl) as Mn^{III}–TPPS was transformed into the diacid H_4–$TPPS^{2-}$ metal-free porphyrin. While no evidence was found for Mn^{II}–TPPS in this pH range, it can be produced by dithionite[6,19] reduction of Mn^{III}–TPPS in base at pH 13 or by pulse radiolysis techniques.[21]

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