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Syntheses, Molecular Structures, and Properties of Two Polar Diruthenium(II,III) Complexes of 2-Hydroxypyridine and 2-Anilinopyridine

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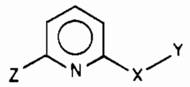
The compounds $Ru_2Cl(hp)_4(Hhp)$ (**8**) and $Ru_2Cl(PhNpy)_4$ (**9**) were prepared by reactions of $Ru_2Cl(CH_3COO)_4$ with Hhp (2-hydroxypyridine) and PhNHpy (2-anilinopyridine) at 120 and 140 °C, respectively. These air-stable compounds have been characterized by analytical and spectroscopic data, and their structures have been determined by X-ray crystallography. Compound **8** crystallizes in the space group $C2/c$ with a = 32.619 (7) Å, b = 10.664 (2) Å, c = 15.099 (4) Å, β = 106.18 (2)°, V = 5044 (2) $Å^3$, and Z = 8. Compound **9** belongs to the space group $C2/c$ with a = 23.529 (9) Å, b = 9.599 (5) Å, c = 21.475 (11) Å, β = 126.26 (3)°, V = 3910 (4) $Å^3$, and Z = 4. Each compound has a totally polar arrangement of the four bridging ligands (i.e., all four are oriented in the same direction) across the diruthenium centers. The metal oxidation states in both the complexes are formally +2 and +3, giving an average value of +2.5. The Ru–Ru distances in **8** and **9** are 2.286 (1) and 2.275 (3) Å, respectively. In **8**, one ruthenium atom is coordinated by all four nitrogen atoms of the bridging ligands and one chlorine atom, while the other ruthenium atom is bonded to five oxygen atoms of five ligands. The axial ligands are a chlorine atom and an Hhp molecule. The Hhp hydrogen atom is bonded to the pyridine nitrogen and is used in hydrogen-bond formation to one of the bridging oxygen atoms. In **9**, one ruthenium atom is bonded to all four pyridine nitrogen atoms (N_{py}) and an axial chlorine atom, while the other ruthenium atom has all four amine nitrogen atoms (N_{am}) in its coordination sphere with no axial ligand. The four Ph groups on the amine nitrogen atoms oriented toward the axial site block the axial position. In **8**, the Ru–Cl and average Ru–N distances are 2.558 (2) and 2.117 Å, respectively. The average Ru–O distance in the bridging ligands is 1.992 Å. The axial Ru–O bond length is 2.299 (5) Å. In **9**, the Ru–Cl, average Ru–N_{py}, and average Ru–N_{am} bond lengths are 2.437 (7), 2.104, and 2.026 Å, respectively. Electronic spectra of compounds **8** and **9** show bands at 480 nm (ϵ 4690 M^{-1} cm^{-1}) and 368 nm in CH_3CN for **8** and at 764 nm (6910) and 415 nm (5770) in CH_2Cl_2 for **9**. Compound **8** has a magnetic moment of 4.61 μ_B in the solid state at 297 K, and **9** has a magnetic moment of 3.94 μ_B in CH_2Cl_2 at 308 K.

Introduction

Unsymmetrical bidentate ligands of type **1**, bridging across a pair of metal atoms, are of considerable interest[1] since they favor the formation of compounds having short metal–metal bonds. Reactivity of such ligands has been extensively studied[1] on Cr, Mo, W, and Rh. In most cases tetracarboxylates were used as starting materials for their synthesis. Recent reports[2–6] from this laboratory have shown that diruthenium and diosmium tetracarboxylates can be used as starting materials in synthesizing various complexes of these elements having strong metal–metal bonds. Since the discovery of the first triply bonded diosmium species, $Os_2Cl_2(hp)_4$,[7] we have reported the molecular structures of several diosmium and diruthenium complexes: $Ru_2(ap)_6(PMe_2Ph)_2$,[2] $Ru_2(Ph)_2(PhCONH)_2[Ph_2POC(Ph)N]_2$,[3] $Os_2Cl_3(PhNpy)_3$,[5] $Os_2Cl_2(O_2CR)_2[Ph_2P(C_6H_4)]_2$,[4] $Os_2Cl_2(PhCONH)_4$.[6] The reaction of $Ru_2Cl(CH_3COO)_4$ with amides is known[3,8] to produce $Ru_2Cl(amidato)_4$, but there is no X-ray structural evidence available. Apart from the tetracarboxylates, the only known[9] diruthenium complex having four ligands bridging across the metal centers is $Ru_2(mhp)_4{\cdot}CH_2Cl_2$, which was obtained in a yield of only 8%. This compound, which is assumed to have a Ru–Ru double bond, with a Ru–Ru bond length of 2.238 (1) Å, is highly air sensitive, although the diruthenium tetracarboxylates are all air stable.

We were particularly interested to investigate the reactions of $Ru_2Cl(CH_3COO)_4$ with other type **1** ligands. Our first choice of ligand was 2-hydroxypyridine, having nitrogen and oxygen atoms available for coordination to the metal center. Second, we choose 2-anilinopyridine as a typical ligand with two nitrogen atoms as donors. Earlier[2] we had attempted, unsuccessfully, to prepare $Ru_2(ap)_4$ (where Hap is 2-aminopyridine) although addition of PMe_2Ph to the reaction mixture gave the novel edge-sharing bioctahedral complex $Ru_2(ap)_6(PMe_2Ph)_2$. However, on changing the reaction conditions, we have been able to isolate two new Ru(II)–Ru(III) dimeric products in almost quantitative yield. Both of these new complexes are indefinitely stable in air.



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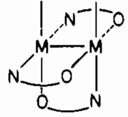
Hhp: X = O; Y = Z = H
Hmhp: X = O; Y = H; Z = CH_3
Hfhp: X = O; Y = H; Z = F
PhNHpy: X = NH; Y = Ph; Z = H
Hmap: X = NH; Y = H; Z = CH_3
Hap: X = NH; Y = Z = H

The compounds that we shall report in this paper have unusual coordination environments. In all of the previously known[7,10] complexes of 2-hydroxypyridine (e.g., in $Os_2Cl_2(hp)_4$) and 2-anilinopyridine (e.g., in $M_2(PhNpy)_4$ (M = Mo, W)), the molecules have coordination arrangements of types **2** and **3**, respectively. In general, complexes of the type $M_2(mhp)_4$ or $M_2(map)_4$ belong[1] to the structural types **2** and **4**. We use N_1 and N_2 to distinguish the different kinds of donor nitrogen atoms in **3** and **4**. In some dirhodium complexes of Hmhp, the partially polar, unsymmetrical ligand arrangement of the type **5** is known[11,12] to



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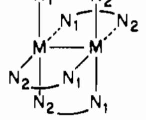

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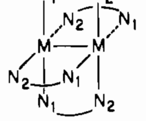

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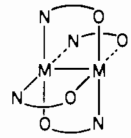

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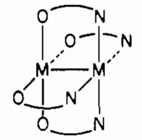

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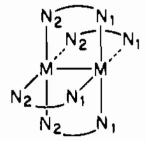

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[1] Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, **1982**.

[2] Chakravarty, A. R.; Cotton, F. A.; Tocher, D. A. *Inorg. Chem.* **1984**, *23*, 4030.

[3] Chakravarty, A. R.; Cotton, F. A.; Tocher, D. A. *J. Am. Chem. Soc.* **1984**, *106*, 6409.

[4] Chakravarty, A. R.; Cotton, F. A.; Tocher, D. A. *J. Chem. Soc., Chem. Commun.* **1984**, 501. Chakravarty, A. R.; Cotton, F. A.; Tocher, D. A. *Inorg. Chem.* **1984**, *23*, 4697.

[5] Chakravarty, A. R.; Cotton, F. A.; Tocher, D. A. *Inorg. Chem.* **1984**, *23*, 4693.

[6] Chakravarty, A. R.; Cotton, F. A.; Tocher, D. A. *Inorg. Chim. Acta* **1984**, *89*, L15.

[7] Cotton, F. A.; Thompson, J. L. *J. Am. Chem. Soc.* **1980**, *102*, 6437.

[8] Malinski, T.; Chang, D.; Feldman, F. N.; Bear, J. L.; Kadish, K. M. *Inorg. Chem.* **1983**, *22*, 3225.

[9] Clegg, W. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, *B36*, 3112.

[10] Chakravarty, A. R.; Cotton, F. A.; Shamshoum, E. S. *Inorg. Chem.* **1984**, *23*, 4216.

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Table I. Crystallographic Data

formula	$Ru_2Cl(C_5H_4NO)_4(C_5H_5NO)$ (8)	$Ru_2Cl(C_{11}H_9N_2)_4$ (9)
fw	709.07	914.42
space group	$C2/c$	$C2/c$
syst abs	hkl ($h + k = 2n$), $h0l$ ($l = 2n, h = 2n$), $0k0$ ($k = 2n$)	hkl ($h + k = 2n$), $h0l$ ($l = 2n, h = 2n$), $0k0$ ($k = 2n$)
a, Å	32.619 (7)	23.529 (9)
b, Å	10.664 (2)	9.599 (5)
c, Å	15.099 (4)	21.475 (11)
α, deg	90.0	90.0
β, deg	106.18 (2)	126.26 (3)
γ, deg	90.0	90.0
V, Å^3	5044 (2)	3910 (4)
Z	8	4
d_{calcd}, g/cm^3	1.871	1.553
cryst size, mm	0.3 × 0.3 × 0.2	0.2 × 0.2 × 0.3
μ(Mo Kα), cm^{-1}	13.3	8.68
data collcn instrum	Syntex P$\bar{1}$	Syntex P$\bar{1}$
radiation (monochromated in incident beam)	Mo Kα ($\lambda = 0.710\,73$ Å)	Mo Kα ($\lambda = 0.710\,73$ Å)
orientation reflcns: no.; range (2θ), deg	15; $17 < 2\theta < 31$	15; $15 < 2\theta < 22$
temp, °C	5	25 ± 2
scan method	ω	ω-2θ
data collcn range (2θ), deg	4-50	5-45
no. of unique data; total with $F_o^2 > 3\sigma(F_o^2)$	1655; 1598	1212; 1087
no. of parameters refined	427	250
R^a	0.029	0.050
$R_w{}^b$	0.038	0.069
quality-of-fit indicator^c	0.964	1.335
largest shift/esd, final cycle	0.95	0.18
largest peak, e/Å^3	1.143	0.74

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

occur. We have found in our new complexes a *totally* polar arrangement of ligands as in 6 and 7. Recent reports[13,14] from this laboratory have described the first examples of such polar arrangements in the 6-fluoro-2-hydroxypyridine complexes of Cr_2, Mo_2, W_2, and Rh_2. Steric considerations were thought to be involved in these fhp complexes. The present hp complex may be of further help in understanding the electronic and steric factors responsible for this type of arrangement. To our knowledge, $Ru_2Cl(PhNpy)_4$ is the first example of a totally polar arrangement in an $M_2(N_1N_2)_4$ complex.

Experimental Section

Materials. $Ru_2(O_2CCH_3)_4Cl$ was prepared by using a literature procedure.[15] The ligands 2-hydroxypyridine (Hhp) and 2-anilinopyridine (PhNHpy) were obtained from Aldrich Chemical Co. The ligands were purified by sublimation prior to use.

Preparations. $Ru_2Cl(hp)_4(Hhp)$ (8). A 0.10-g quantity of $Ru_2(O_2CCH_3)_4Cl$ and 5.0 g of Hhp were heated under a dinitrogen atmosphere at 120 °C for 72 h. At this temperature the ligand was in molten condition. Excess Hhp ligand was sublimed off under vacuum at 120 °C, and the residue, which was red, was washed several times with methanol and diethyl ether. The yield was quantitative. The compound is slightly soluble in CH_2Cl_2, Me_2SO, CH_3CN, and CH_3OH. Dark red single crystals, suitable for X-ray study, were obtained by slow evaporation of an acetonitrile solution of the compound. Anal. Calcd for $Ru_2ClO_5N_5C_{25}H_{21}$: C, 42.34, H, 2.96; N, 9.88. Found: C, 42.61; H, 3.11; N, 9.95. IR (KBr phase): 3060 (br), 1660 (s), 1605 (s), 1580 (s), 1530 (s), 1460 (s), 1425 (s), 1405 (s), 1345 (s), 1270 (s), 1150 (s), 1110 (m), 1035 (m), 1015 (m), 995 (m), 885 (s), 770 (s), 740 (m), 655 (m), 618 (s), 588 (m), 580 (m), 525 (w), 515 (w), 478 (w), 468 (w), 442 (w), 348 (s), 308 (m) cm^{-1}. (Key: s, strong; m, medium; w, weak, and br, broad.) Electronic spectrum (900–340 nm, CH_3CN solvent): λ_{max} 480 nm (ϵ 4690 M^{-1} cm^{-1}), 368 (sh).

$Ru_2(PhNpy)_4Cl$ (9). A 0.10-g quantity of $Ru_2(O_2CCH_3)_4Cl$ was heated together with 0.15 g of the ligand 2-anilinopyridine at 140 °C for 2 h. The molten mixture was then heated under vacuum for a further 1 h to remove unreacted ligand, and the remaining dark green mass was then extracted with methylene chloride. The solution was filtered and then allowed to evaporate slowly, affording a homogeneous mass of dark green crystalline material, yield 0.14 g (73%). Anal. Calcd for $Ru_2ClN_8C_{44}H_{36}$: C, 57.77, H, 3.94. Found: C, 57.79, H, 3.95. IR (Nujol mull, CsI plates): 1592 (s), 1582 (s), 1531 (m), 1285 (s), 1265 (w), 1256 (w), 1228 (w), 1217 (s), 1169 (w) 1155 (m), 1110 (w), 1070 (m), 1042 (w), 1017 (s), 952 (w), 914 (s), 861 (s), 752 (s), 735 (m), 696 (s), 673 (w), 649 (w), 606 (w), 538 (w), 502 (s), 439 (m), 381 (s), 325 (w), 311 (s), 286 (w), 244 (m) cm^{-1}. (Key: s, strong; m, medium; w, weak.) Electronic spectrum (900–340 nm, CH_2Cl_2 solvent): λ_{max} 764 nm (ϵ 6910 M^{-1} cm^{-1}), 415 (ϵ 5770). Magnetic moment (CH_2Cl_2) $\mu_{eff} = 3.94\ \mu_B$ at ca. 25 °C.

Measurements. The elemental analyses were obtained from Galbraith Laboratories, Inc. The infrared spectra were taken with a Perkin-Elmer 785 spectrophotometer. Electronic spectra were recorded on a Cary 17D spectrophotometer. Magnetic measurements on $Ru_2Cl(PhNpy)_4$ were made in solution by the Evans method by using a Varian EM 390 spectrometer. The susceptibility of solid $Ru_2Cl(hp)_4(Hhp)$ was measured by the Faraday method on a balance at Abilene Christian University through the kindness of Prof. Bennett Hutchinson: $\chi_g = 12.11 \times 10^{-6}$ cgsu at 297 K. With a diamagnetic correction of 351 cgsu, a corrected molar susceptibility of 8930 × 10^{-6} and a μ_{eff} of 4.61 μ_B were calculated.

X-ray Crystallographic Procedures. The structures of the single crystals of 8 and 9 were determined by using general procedures described elsewhere.[16,17] A detailed description pertinent to these compounds is available as supplementary material. In each case the centric ($C2/c$) space group was chosen in preference to the noncentric one (Cc) on the basis of the satisfactory refinement. Crystallographic data and other basic information pertaining to the data collection are summarized in Table I. Complete tables of bond distances and angles as well as anisotropic thermal parameters and structure factors are available as supplementary material.

Results and Discussion

Preparation and Chemistry. Both compounds were prepared in very high yield by reacting $Ru_2Cl(CH_3COO)_4$ with molten ligand at elevated temperature. This preparative route is par-

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(11) Cotton, F. A.; Felthouse, T. R. *Inorg. Chem.* **1981**, *20*, 584.

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

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

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

(15) Stephenson, T. A.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1966**, *28*, 2285.

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

(17) 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. S. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr. Theor. Gen. Crystallogr.* **1968**, *A24*, 351.

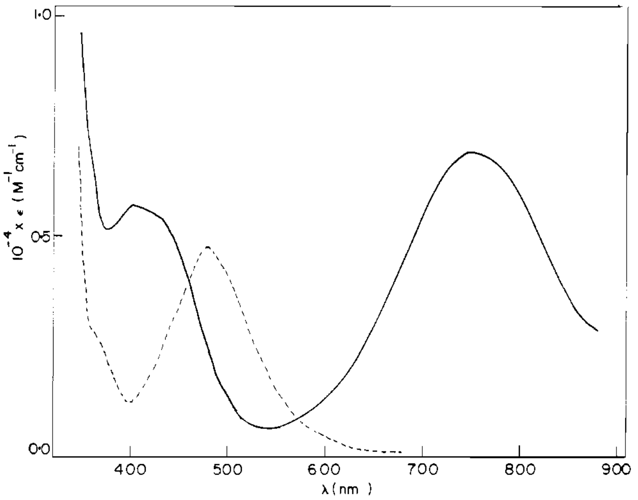


Figure 1. Electronic spectra of $Ru_2Cl(PhNpy)_4$ (—) in CH_2Cl_2 and $Ru_2Cl(hp)_4(Hhp)$ (---) in CH_3CN.

ticularly useful when the replaceable hydrogen is acidic enough to undergo exchange with the acetate of the starting material. In the preparation of complexes of type $M_2(NX)_4$, where M = Cr, Mo, and W and NX is a type **1** ligand, a technique commonly employed has been to react the starting material with the lithium salt of the ligand. The advantage in this process is that lithium salt is more reactive than the free ligand. However, this procedure is not effective in the case of ruthenium and osmium. One possible explanation for this is that the lithium first removes the axial halides from the $M_2(O_2CR)_4Cl_x$ molecules, thus giving an intractible reaction mixture. To date, there is no report of success with such a reaction to prepare a $M_2(NX)_4Cl_x$ type compound of ruthenium or osmium. However, by employing this type of reaction, we have recently discovered[2] the novel compound $Ru_2(ap)_6(PMe_2Ph)_2$.

The present complexes, **8** and **9**, are obtained by using reaction conditions similar to those used[3,8] in the preparation of $Ru_2Cl(RCONH)_4$. The product is homogeneous and pure (vide elemental analysis), and there is quantitative replacement of all four acetates by hp and PhNpy. Both of the new complexes reported here are air stable for an indefinite period.

The complex $Ru_2Cl(hp)_4(Hhp)$ is red and slightly soluble in CH_2Cl_2, Me_2SO, CH_3CN and MeOH to give red solutions but insoluble in benzene, hexane, and diethyl ether. The $Ru_2Cl(PhNpy)_4$ complex is green and moderately soluble in common organic solvents to give green solutions. Magnetic measurements for the latter, done in CH_2Cl_2 solution by using Evans' method[18] (μ_{eff} value of 3.94 μ_B at ca. 25 °C), indicate the presence of three unpaired spins per dinuclear molecule. Because of its insolubility, $Ru_2Cl(hp)_4(Hhp)$ was measured in the solid state (μ_{eff} at ca. 25 °C is 4.61 μ_B). Similar magnetic moments were observed[19] in $Ru_2(O_2CR)_4Cl$. The formal oxidation states of the metal atoms are +2 ($4d^6$) and +3 ($4d^5$), so that for a valence-trapped situation we would expect a magnetic moment due to one unpaired spin. However, orbital energies calculated for $[Ru_2(O_2CH)_4]^+$ and its derivatives by the SCF–Xα–SW method show[20] that there is strong Ru–Ru bonding, resulting in an MO pattern in which two π^* and one δ^* are almost degenerate. This gives rise to an electronic configuration of $(\sigma)^2(\pi)^4(\delta)^2(\pi^*)^2(\delta^*)^1$ instead of $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^2(\pi^*)^1$.

The electronic spectra of **8** and **9** are shown in Figure 1. In CH_3CN, $Ru_2Cl(hp)_4(Hhp)$ exhibits a strong absorption at 480 nm (ε 4690 M^{-1} cm^{-1}). In addition, there is a shoulder at 368 nm. In a CH_2Cl_2 solution of $Ru_2Cl(PhNpy)_4$, two strong absorption bands occur at 764 nm (ε 6910 M^{-1} cm^{-1}) and 415 nm (5770).

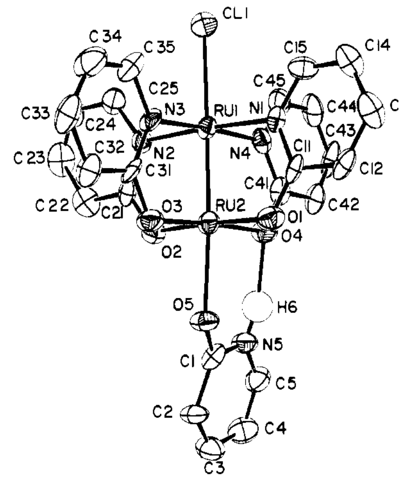
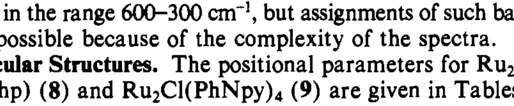


Figure 2. ORTEP representation of the $Ru_2Cl(hp)_4(Hhp)$ molecule. Thermal ellipsoids are at the 50% probability level. The atom-numbering scheme is defined.

Diruthenium tetracarboxylates exhibit absorption bands near 500 nm. SCF–Xα–SW calculations by Norman and his coworkers[20] on $Ru_2(O_2CR)_4^+$ led them to propose that the band near 500 nm is due to a $\pi(O) \rightarrow \pi^*(RuRu)$ transition. The weak band near 1000 nm in the aqueous solution spectrum was assigned[20] to the $\delta \rightarrow \delta^*$ transition. In $Ru_2(HNOCCF_3)_4Cl$, absorptions are known[8] to occur at 423 and 463 (sh) nm in CH_2Cl_2. The low-energy band was assigned to a Cl^- to metal charge-transfer transition.

Comparison of the spectral data of **8** and **9** shows there is a considerable red-shift on going from hp to PhNpy. The 415-nm band in **9** is broad and may involve more than one transition (Figure 1). The spectral features observed in our compounds are totally different from those found in $Ru_2(HNOCCF_3)_4Cl$, and without any theoretical treatment of the electronic structures of these new compounds, it is not worthwhile to discuss assignments.

The infrared spectra of $Ru_2Cl(hp)_4(Hhp)$ and $Ru_2Cl(PhNpy)_4$ show characteristic bands of the ligands (see Experimental Section). The compound $Ru_2Cl(hp)_4(Hhp)$ does not show any sharp band due to N–H stretching, but instead a broad band was observed near 3060 cm^{-1}. The absence of an N–H stretch would suggest involvement of the N–H group in strong hydrogen bonding, O···H–N. The presence of such a hydrogen bond is confirmed by X-ray crystallography. In the IR spectrum of this compound there is a strong band at 1660 cm^{-1}, which may be considered consistent with the presence of the keto form **11** of 2-hydroxypyridine.



10 **11a** **11b**

The presence of such a tautomeric form is also suggested by the structural data. The IR spectrum of $Ru_2Cl(PhNpy)_4$ does not have any N–H stretch, indicating the presence of all ligands in the anionic form. The stretches observed at 308 and 311 cm^{-1} in $Ru_2Cl(hp)_4(Hhp)$ and in $Ru_2Cl(PhNpy)_4$, respectively, can be tentatively assigned to Ru–Cl stretches. Several bands were observed in the range 600–300 cm^{-1}, but assignments of such bands are not possible because of the complexity of the spectra.

Molecular Structures. The positional parameters for $Ru_2Cl(hp)_4(Hhp)$ (**8**) and $Ru_2Cl(PhNpy)_4$ (**9**) are given in Tables II and III, respectively. Table IV gives selected bond distances and angles for $Ru_2Cl(hp)_4(Hhp)$, and an ORTEP plot of this compound is presented in Figure 2. Selected bond distances and angles for $Ru_2Cl(PhNpy)_4$ are given in Table V, and Figure 3 is the ORTEP diagram of this molecule.

The most noteworthy feature in the complexes is the arrangement of ligands across the metal centers. Both of them show a totally polar arrangement of ligands, an arrangement previously known[13,14] only in the fhp complexes of Cr_2, Mo_2, W_2, and Rh_2.

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[18] Evans, D. F. *J. Chem. Soc.* **1959**, 2003.

[19] Cotton, F. A.; Pedersen, E. *Inorg. Chem.* **1975**, *14*, 388.

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

Table II. Table of Positional Parameters and Their Estimated Standard Deviations for $Ru_2Cl(hp)_4(Hhp)$ (8)

atom	x	y	z	B,[a] Å^2	atom	x	y	z	B,[a] Å^2
Ru(1)	0.89946 (2)	0.22158 (7)	0.04109 (5)	2.25 (1)	C(33)	1.0093 (3)	0.544 (1)	0.1264 (6)	4.0 (2)
Ru(2)	0.85223 (2)	0.38232 (7)	−0.00920 (5)	2.42 (1)	C(34)	1.0192 (3)	0.420 (1)	0.1474 (7)	4.5 (3)
Cl(1)	0.95193 (8)	0.0400 (2)	0.0945 (2)	3.94 (6)	C(35)	0.9893 (3)	0.329 (1)	0.1246 (7)	3.8 (2)
O(1)	0.8452 (2)	0.4108 (5)	0.1161 (4)	3.1 (1)	C(41)	0.8065 (3)	0.1447 (8)	−0.0289 (5)	2.9 (2)
O(2)	0.8557 (2)	0.3607 (5)	−0.1372 (4)	3.1 (1)	C(42)	0.7707 (3)	0.0642 (9)	−0.0510 (6)	3.4 (2)
O(3)	0.8985 (2)	0.5089 (5)	0.0154 (4)	3.4 (2)	C(43)	0.7758 (3)	−0.059 (1)	−0.0384 (6)	4.3 (2)
O(4)	0.8017 (2)	0.2650 (5)	−0.0380 (4)	3.2 (1)	C(44)	0.8167 (3)	−0.1097 (8)	−0.0061 (6)	4.2 (2)
O(5)	0.8070 (2)	0.5467 (5)	−0.0670 (4)	3.0 (1)	C(45)	0.8502 (3)	−0.0302 (8)	0.0138 (6)	3.6 (2)
N(1)	0.8886 (2)	0.2406 (6)	0.1722 (4)	2.4 (2)	H(2)	0.772 (3)	0.727 (8)	−0.154 (6)	5*
N(2)	0.9088 (2)	0.2176 (6)	−0.0910 (4)	2.5 (2)	H(3)	0.701 (3)	0.733 (8)	−0.263 (6)	5*
N(3)	0.9481 (2)	0.3577 (7)	0.0790 (4)	2.5 (2)	H(4)	0.666 (3)	0.548 (8)	−0.283 (5)	5*
N(4)	0.8466 (2)	0.0941 (6)	0.0028 (4)	2.7 (2)	H(5)	0.695 (3)	0.356 (8)	−0.205 (6)	5*
N(5)	0.7479 (2)	0.4417 (7)	−0.1479 (5)	3.1 (2)	H(6)	0.760 (3)	0.367 (8)	−0.117 (6)	5*
C(1)	0.7718 (3)	0.5480 (8)	−0.1284 (5)	2.6 (2)	H(12)	0.843 (3)	0.411 (8)	−0.271 (5)	5*
C(2)	0.7532 (3)	0.6590 (8)	−0.1763 (6)	3.1 (2)	H(13)	0.873 (3)	0.292 (8)	0.393 (6)	5*
C(3)	0.7139 (3)	0.6533 (9)	−0.2342 (6)	3.8 (2)	H(14)	0.915 (3)	0.144 (8)	0.373 (5)	5*
C(4)	0.6899 (3)	0.544 (1)	−0.2502 (6)	4.0 (3)	H(15)	0.922 (3)	0.102 (8)	0.228 (6)	5*
C(5)	0.7078 (3)	0.4405 (9)	−0.2087 (6)	3.6 (2)	H(22)	0.875 (2)	0.350 (8)	−0.287 (6)	5*
C(11)	0.8636 (2)	0.3387 (8)	0.1837 (6)	2.6 (2)	H(23)	0.924 (3)	0.178 (8)	−0.317 (6)	5*
C(12)	0.8576 (3)	0.3572 (8)	0.2737 (6)	2.9 (2)	H(24)	0.970 (3)	0.107 (8)	−0.211 (6)	5*
C(13)	0.8759 (3)	0.2797 (9)	0.3429 (6)	3.9 (2)	H(25)	0.957 (3)	0.087 (8)	−0.059 (5)	5*
C(14)	0.9004 (3)	0.1809 (9)	0.3288 (6)	3.8 (2)	H(32)	0.961 (2)	0.659 (8)	0.062 (5)	5*
C(15)	0.9061 (3)	0.1637 (8)	0.2434 (6)	3.1 (2)	H(33)	1.032 (3)	0.606 (8)	0.142 (6)	5*
C(21)	0.8842 (3)	0.2909 (8)	−0.1579 (5)	2.6 (2)	H(34)	1.049 (3)	0.404 (8)	0.181 (5)	5*
C(22)	0.8890 (3)	0.2915 (9)	−0.2482 (6)	3.6 (2)	H(35)	0.991 (3)	0.234 (8)	0.137 (6)	5*
C(23)	0.9201 (3)	0.2151 (9)	−0.2664 (6)	4.0 (2)	H(42)	0.744 (3)	0.093 (8)	−0.082 (5)	5*
C(24)	0.9455 (3)	0.1454 (8)	−0.1994 (6)	3.7 (2)	H(43)	0.753 (3)	−0.099 (8)	−0.057 (6)	5*
C(25)	0.9393 (3)	0.1457 (8)	−0.1132 (6)	3.3 (2)	H(44)	0.820 (3)	−0.191 (8)	0.004 (6)	5*
C(31)	0.9372 (2)	0.4794 (8)	0.0575 (5)	2.5 (2)	H(45)	0.878 (3)	−0.057 (9)	0.036 (6)	5*
C(32)	0.9682 (3)	0.5752 (9)	0.0804 (6)	3.3 (2)					

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

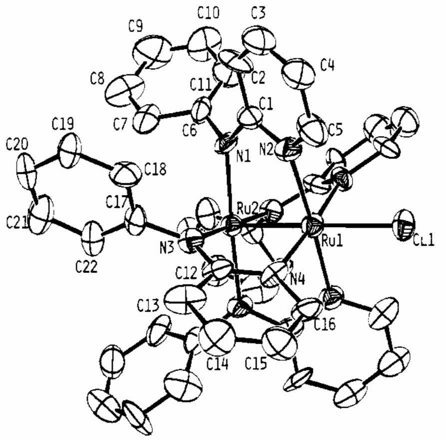

Figure 3. ORTEP drawing of the $Ru_2Cl(PhNpy)_4$ molecule. Atoms are represented by thermal vibration ellipsoids at the 50% level, and the atom-labeling scheme in this molecule is defined.

In $Ru_2Cl(hp)_4(Hhp)$ one ruthenium atom is bonded to four pyridine nitrogen atoms and one axial chlorine atom while the other ruthenium atom is coordinated by four oxygen atoms of the bridging hp ligands along with an axial Hhp ligand coordinated through the oxygen atom. In $Ru_2Cl(PhNpy)_4$, one metal atom is coordinated by four pyridine nitrogen atoms and one axial chlorine atom as in **8** while the other ruthenium center is coordinated by four amine nitrogen atoms. The axial position of this metal atom is hemmed in by the four pendant phenyl groups attached to the amine nitrogen atoms. The metal–metal bond lengths in **8** and **9** are 2.286 (1) and 2.275 (3) Å, respectively. These values are in the range of 2.27–2.29 Å found[21] in $Ru_2(O_2CR)_4Cl$ complexes. While the molecule **8** does not have any symmetry, **9** has a twofold axis that coincides with the Cl(1)–Ru(1)–Ru(2) axis.

Table III. Table of Positional Parameters and Their Estimated Standard Deviations for $Ru_2Cl(PhNpy)_4$ (9)

atom	x	y	z	B,[a] Å^2
Ru(1)	0.500	0.2460 (3)	0.750	2.70 (4)
Ru(2)	0.500	0.0089 (2)	0.750	2.46 (4)
Cl(1)	0.500	0.4999 (7)	0.750	3.4 (2)
N(1)	0.5387 (5)	0.013 (1)	0.6873 (5)	3.0 (3)
N(2)	0.4971 (5)	0.240 (2)	0.6502 (5)	3.3 (3)
N(3)	0.4003 (5)	0.012 (3)	0.6513 (6)	2.9 (3)
N(4)	0.3893 (5)	0.236 (1)	0.6808 (5)	2.9 (3)
C(1)	0.5247 (7)	0.122 (2)	0.6400 (7)	3.4 (4)
C(2)	0.5327 (7)	0.117 (2)	0.5799 (7)	4.3 (4)
C(3)	0.5062 (8)	0.229 (2)	0.5285 (9)	5.1 (5)
C(4)	0.4753 (8)	0.348 (2)	0.5368 (8)	5.1 (6)
C(5)	0.4722 (8)	0.350 (2)	0.5993 (8)	4.6 (5)
C(6)	0.5843 (7)	−0.092 (2)	0.6947 (7)	3.2 (5)
C(7)	0.5591 (8)	−0.234 (2)	0.6758 (7)	4.3 (5)
C(8)	0.6064 (9)	−0.343 (2)	0.6890 (9)	6.3 (6)
C(9)	0.6726 (9)	−0.309 (2)	0.711 (7)	7.1 (7)
C(10)	0.6992 (8)	−0.174 (2)	0.733 (1)	6.0 (6)
C(11)	0.6557 (8)	−0.067 (2)	0.724 (1)	5.9 (6)
C(12)	0.3578 (6)	0.123 (2)	0.6378 (7)	3.2 (4)
C(13)	0.2824 (7)	0.112 (2)	0.5827 (8)	4.2 (5)
C(14)	0.2437 (8)	0.224 (2)	0.5802 (9)	5.2 (6)
C(15)	0.2767 (7)	0.342 (2)	0.6270 (9)	4.7 (6)
C(16)	0.3507 (7)	0.348 (2)	0.6770 (8)	3.7 (4)
C(17)	0.3766 (7)	−0.098 (2)	0.5970 (8)	3.1 (5)
C(18)	0.3621 (7)	−0.062 (2)	0.5232 (7)	3.8 (5)
C(19)	0.3422 (9)	−0.172 (2)	0.4701 (9)	5.8 (6)
C(20)	0.3344 (9)	−0.308 (2)	0.486 (1)	4.8 (5)
C(21)	0.3491 (9)	−0.335 (2)	0.5574 (9)	5.1 (6)
C(22)	0.3686 (7)	−0.232 (2)	0.6111 (8)	4.1 (5)

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

The molecule $Ru_2(hp)_4(Hhp)$ can be viewed as two dissimilar octahedra connected through a metal–metal bond. The Ru(1) atom is bonded to Cl(1) and four nitrogen atoms, with the Ru–Cl

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[21] (a) Bennett, M. J.; Caulton, K. G.; Cotton, F. A. *Inorg. Chem.* **1969**, *8*, 1. (b) Bino, A.; Cotton, F. A.; Felthouse, T. R. *Inorg. Chem.* **1979**, *18*, 2599. (c) Togano, T.; Mukaida, M.; Nomura, T. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2085. (d) Martin, D. S.; Newman, R. A.; Vlasnik, L. M. *Inorg. Chem.* **1980**, *19*, 3404.

Table IV. Selected Bond Distances and Angles for $Ru_2Cl(hp)_4(Hhp)$ (8)[a]

	Bond Distances (Å)		
Ru(1)-Ru(2)	2.286 (1)	O(4)-C(41)	1.293 (10)
-Cl(1)	2.558 (2)	-H(6)	1.89 (8)
-N(1)	2.115 (7)	O(5)-C(1)	1.257 (9)
-N(2)	2.100 (7)	N(1)-C(11)	1.366 (11)
-N(3)	2.107 (7)	-C(15)	1.346 (10)
-N(4)	2.144 (7)	N(2)-C(21)	1.350 (9)
Ru(2)-O(1)	1.992 (6)	-C(25)	1.368 (12)
-O(2)	1.981 (6)	N(3)-C(31)	1.358 (11)
-O(3)	1.980 (6)	-C(35)	1.363 (11)
-O(4)	2.016 (6)	N(4)-C(41)	1.371 (11)
-O(5)	2.299 (5)	-C(45)	1.335 (11)
O(1)-C(11)	1.284 (9)	N(5)-C(1)	1.360 (11)
O(2)-C(21)	1.294 (11)	-C(5)	1.373 (10)
O(3)-C(31)	1.284 (9)	-H(6)	0.95 (8)
		O(4)-N(5)	2.78
	Bond Angles (deg)		
Ru(2)-Ru(1)-Cl(1)	178.97 (6)	Ru(1)-Ru(2)-O(3)	92.2 (2)
-N(1)	88.1 (2)	-O(4)	92.5 (2)
-N(2)	87.8 (2)	-O(5)	176.3 (2)
-N(3)	87.8 (2)	Cl(1)-Ru(1)-N(1)	92.8 (2)
-N(4)	88.1 (2)	-N(2)	91.3 (2)
Ru(1)-Ru(2)-O(1)	92.5 (2)	-N(3)	92.7 (2)
-O(2)	91.2 (2)	-N(4)	91.4 (2)
O(5)-Ru(2)-O(1)	90.7 (2)	Ru(1)-N(3)-C(31)	117.6 (5)
-O(2)	85.6 (2)	-C(35)	123.1 (6)
-O(3)	85.9 (2)	Ru(1)-N(4)-C(41)	117.6 (5)
-O(4)	89.4 (2)	-C(45)	123.8 (5)
N(1)-Ru(1)-N(2)	175.5 (3)	Ru(2)-O(1)-C(11)	120.7 (6)
-N(3)	89.4 (3)	-O(2)-C(21)	122.9 (5)
-N(4)	88.9 (3)	-O(3)-C(31)	121.3 (5)
N(2)-Ru(1)-N(3)	88.5 (3)	-O(4)-C(41)	121.6 (5)
-N(4)	92.9 (3)	-O(5)-C(1)	130.2 (5)
N(3)-Ru(1)-N(4)	175.6 (3)	C(11)-N(1)-C(15)	119.9 (8)
O(1)-Ru(2)-O(2)	176.1 (2)	C(21)-N(2)-C(25)	117.5 (7)
-O(3)	90.1 (3)	C(31)-N(3)-C(35)	119.3 (7)
-O(4)	89.8 (3)	C(41)-N(4)-C(45)	118.4 (7)
O(2)-Ru(2)-O(3)	90.8 (3)	C(1)-N(5)-C(5)	122.4 (7)
-O(4)	89.0 (3)	C(1)-N(5)-H(6)	117 (5)
O(3)-Ru(2)-O(4)	175.3 (2)	C(5)-N(5)-H(6)	120 (5)
Ru(1)-N(1)-C(11)	117.0 (5)	O(4)-H(6)-N(5)	157 (8)
-C(15)	123.1 (6)		
Ru(1)-N(2)-C(21)	119.1 (6)		
-C(25)	123.4 (5)		

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

Table V. Some Important Bond Distances (Å) and Angles (deg) in $Ru_2Cl(PhNpy)_4$ (9)[a]

	Bond Distances (Å)		
Ru(1)-Ru(2)	2.275 (3)	N(1)-C(1)	1.36 (2)
-Cl(1)	2.437 (7)	-C(6)	1.42 (2)
-N(2)	2.105 (11)	N(2)-C(1)	1.38 (2)
-N(4)	2.102 (12)	N(3)-C(12)	1.36 (2)
Ru(2)-N(1)	2.023 (12)	-C(17)	1.42 (2)
-N(3)	2.028 (12)	N(4)-C(12)	1.34 (2)
	Bond Angles (deg)		
Ru(2)-Ru(1)-Cl(1)	180.00 (0)	N(1)-Ru(2)-N(1)′	177.6 (9)
-N(2)	88.3 (5)	N(3)-Ru(2)-N(3)′	178.1 (9)
-N(4)	87.5 (5)	Ru(1)-N(2)-C(1)	117 (1)
Ru(1)-Ru(2)-N(1)	88.8 (4)	-C(5)	122 (1)
-N(3)	89.1 (4)	-N(4)-C(16)	120 (1)
Cl(1)-Ru(1)-N(2)	91.7 (5)	-C(12)	118 (1)
-N(4)	92.5 (5)	Ru(2)-N(1)-C(6)	121 (1)
N(1)-Ru(2)-N(3)	90.2 (5)	-C(1)	121 (1)
N(2)-Ru(1)-N(4)	89.9 (5)	-N(3)-C(12)	119 (1)
N(2)-Ru(1)-N(2)′	177 (1)	-C(17)	120 (1)
N(4)-Ru(1)-N(4)′	175.0 (9)		

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

Table VI. Selected Torsional Angles for $Ru_2Cl(hp)_4(Hhp)$ (8) and $Ru_2Cl(PhNpy)_4$ (9)

compd	atom 1	atom 2	atom 3	atom 4	angle, deg
$Ru_2Cl(hp)_4(Hhp)$	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
	O(5)	C(1)	N(5)	H(6)	4.0
$Ru_2Cl(PhNpy)_4$	N(2)	Ru(1)	Ru(2)	N(1)	22.8
	N(4)	Ru(1)	Ru(2)	N(3)	22.6

and average Ru–N distances being 2.558 (2) and 2.117 [10] Å, respectively. The Ru–N bond lengths are in the range 2.100 (7)–2.144 (7) Å. The Ru–Ru–N angles lie in the range 87.8–88.1° while the Ru–Ru–Cl angle is 178.97 (6)°. The Ru–Cl bond lengths found[21] in $Ru_2(O_2CR)_4Cl$ compounds lie in the range 2.57–2.59 Å. The other ruthenium atom, Ru(2), is coordinated by five oxygen atoms. The average Ru–O distance for the bridging ligands is 1.992 [8] Å. The axial Ru–O bond length, 2.299 (5) Å, is considerably longer than the equatorial Ru–O bonds. Such lengthening of the Ru–O bond is expected if the oxygen is the neutral >C=O functionality instead of >C—O⁻.

All of the hydrogen atoms in **8** have been located from difference Fourier maps, and their positional parameters have been refined while keeping the isotropic thermal parameters fixed at 5.0 throughout the refinement. The detection of one hydrogen atom at 0.95 (8) Å from nitrogen atom N(5) of the axial ligand confirms that the axial ligand is neutral. The O(4)–N(5) distance is 2.78 Å, which is in accord with the existence of the hydrogen bond, O(4)···H(6)–N(5), of moderate strength. The O(4)···H(6) distance is 1.89 (8) Å. The C(1)–O(5) distance, 1.257 (9) Å, appears to be somewhat shorter than the other four C–O distances, whose mean value is 1.289 [3] Å, although the difference, 0.032 (9) Å, is not large. Such a difference is consistent with the preponderance of form **10** as a representation of this ligand molecule, with perhaps some contribution from **11** also. The axial mode of coordination of Hhp in **8** is unusual but not unprecedented. In $Rh_2(mhp)_4(Hmhp)$ there is a similar occurrence.[12]

It is to be noted that the Ru(2)–O(4) bond in **8** is considerably longer than the other three equatorial Ru–O bonds. This may be attributed to the participation of O(4) in the hydrogen bond to the axial Hhp ligand. The Ru(1)–Ru(2)–O(5) angle is 176.3 (2)°. The other Ru–Ru–O angles lie in the range 91.3 (2)–92.8 (2)°. While the Ru–Ru–N(1–4) angles are all slightly acute, the Ru–Ru–O(1–4) angles are all slightly obtuse. The presence of the axial Cl atom on Ru(1) would tend to make all Cl–Ru(1)–N(1–4) angles obtuse (ranges from 91.3 (2) to 92.8 (2)°), which in turn would tend to make all Ru–Ru–O(1–4) angles obtuse as well.

The N-C bond lengths in **8** are in the range 1.335 (11)–1.373 (10) Å. The Ru–N–C angles are in the range 117.0 (5)–123.8 (5)°, and Ru–O–C angles are in the range 120.7 (6)–122.9 (5)°, with only Ru(2)–O(5)–C(1) being 130.2 (5)°. The O(4)···H(6)–N(5) angle is 157 (8)°.

The torsion angles about the metal–metal bond are given in Table VI for both compounds. For **8** they lie in the range of 3.4–7.3°, which is similar to the average torsional angle found in $Os_2(hp)_4Cl_2$, viz., 5.5°. In the axial Hhp ligand the atoms O(5)–C(1)–N(5)–H(6)–O(4) are essentially coplanar.

Turning now to the $Ru_2Cl(PhNpy)_4$ molecule, we find that one ruthenium atom has four equatorial nitrogen atoms and an axial chlorine atom, while the other ruthenium atom has only four equatorial nitrogen atoms (Figure 3). As in the case of $Ru_2Cl(hp)_4(Hhp)$, the same feature of unidirectional ligand orientation is present in this molecule. All the phenyl groups of the amine nitrogen atoms are pointed toward the axial position of one ruthenium atom and would appear to effectively block any incoming nucleophile along this direction.

One remarkable feature of this molecule is the unusually short Ru(1)–Cl(1) bond, 2.437 (7) Å. In $Ru_2Cl(O_2CR)_4$ compounds[21] these bond lengths are typically about 2.56 Å, and in **8** the distance was 2.558 (2) Å. The Ru(2)–Ru(1)–Cl(1) angle is required by symmetry to be 180°.

The Ru(2) atom has four equatorial amine nitrogen atoms and a vacant axial site. If we assume that the negative charge of the

Inorg. Chem. **1985**, *24*, 177–181

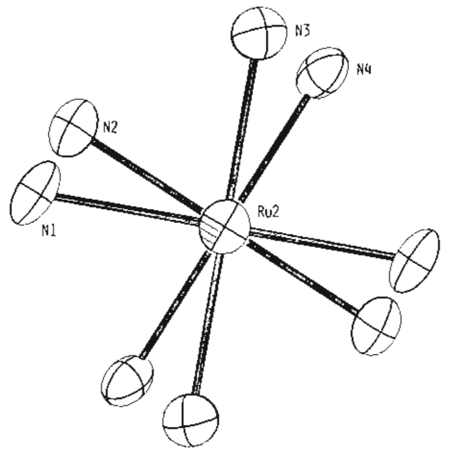

Figure 4. View down the Ru(1)–Ru(2) axis in $Ru_2Cl(PhNpy)_4$ showing the conformation of the eight equatorial atoms coordinated to the diruthenium unit.

$PhNpy^-$ ion tends to reside primarily on the amine nitrogen atom N_{am}, we might expect the Ru–N_{am} bond length to be shorter than the Ru–N_{py} distances, and this is indeed the case. The Ru–N_{am} distances are about 0.08 Å shorter than the Ru–N_{py} distances. In the $M_2(PhNpy)_4$ molecules[10] (M = Mo, W) there was also a difference in the same direction, but it was very much smaller, viz., about 0.02 Å. It would thus appear that some factor other than charge distribution in the ligand must be at work. Probably, the lack of an axial ligand on Ru(2) permits the closer approach of the four equatorial ligands.

The unusual arrangement of ligands in **9** engenders rather large torsion angles about the Ru–Ru bond, as shown in Figure 4 and presented in Table VI. The torsional angles, N(2)–Ru(1)–Ru(2)–N(1) and N(4)–Ru(1)–Ru(2)–N(3), are 22.8 and 22.6°, respectively. In the previously known complexes of 2-anilinopyridine, which are all of the structural type **3**, no significant twists were seen.

Concluding Comments. These two new examples of the totally polar mode of coordination of unsymmetrical bidentate ligands across M–M bonds demonstrate that such arrangements are probably not as rare or unlikely as had been assumed only a little while ago. The question of what factors favor the occurrence of such an arrangement is now of greater importance since the phenomenon is now less of an oddity. A combination of both steric and bonding factors would seem to be operative in all cases.

Perhaps the most straightforward case is present in compound **9**. If there is a strong tendency for the Ru_2^{5+} core to have a Cl^- ion coordinated at one axial position, then once this is done there is a strong steric factor disfavoring the coordination of a Ph–N–nitrogen atom to the same metal atom. Since there is room for all four phenyl groups at the other end, provided some torsion about the Ru–Ru bond occurs, such an arrangement is adopted. In this way one very good axial Ru–Cl bond can be formed without a major penalty (since the Ru–Ru bond has no rotational barrier), whereas for a bridging ligand set of type **3** or **4** a strong Ru–Cl bond might not be possible at either end.

In the case of **8**, it seems that steric factors alone may favor the observed arrangement, but not very decisively. The axial bridging of the Hhp molecule, supported by the hydrogen bond, may well be a stabilizing factor. Its presence may then favor an orientation of the other three hp ligands that are not hydrogen bonded that keeps their bulky pyridine rings away from the axial Hhp molecule. However, there must also be some repulsive force between the C(*n*5)–H groups of these rings and the axial chlorine atom at the other end. The net result of this trade-off would not seem to be immediately obvious.

Finally, in the $M_2(fhp)_4THF$ molecules (M = Cr, Mo, W, Rh), the balance of steric forces would again seem to be a close one. With all fhp ligands directed one way, one metal atom can form one very good M–THF axial bond, whereas, if two fhp bonds were directed each way, both ends of the M_2 unit might be sufficiently encumbered as to allow only very weak M–THF interactions.

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Registry No. **8**, 94089-98-2; **9**, 94089-99-3; $Ru_2(O_2CCH_3)_4Cl$, 38833-34-0.

Supplementary Material Available: Details of the crystal structure determination and listings of angles, anisotropic thermal parameters, distances, and observed and calculated structure factors (46 pages). Ordering information is given on any current masthead page.

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δ → δ* Transition Energies as a Function of δ-Bond Strength: An Extrapolative Assessment of the Ground-State Electron Correlation Energy

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The structural characterization of two partially staggered $Mo_2X_4(LL)_2$ compounds is reported, and their relevance to the relationship between δ → δ* transition energy and torsional twist in quadruply bonded molybdenum dimers is discussed. A second crystallographic form of β-$Mo_2Cl_4(dmpe)_2$ has been subjected to X-ray crystallographic analysis and will be designated as β′-$Mo_2Cl_4(dmpe)_2$ (**1**). It crystallizes in space group $P4_22_12$ with $a = b = 12.124$ [5] Å, $c = 8.805$ (2) Å, $V = 1294$ (1) Å^3, and $Z = 2$. In addition, an analogous bromo compound, β-$Mo_2Br_4(dmpe)_2$ (**2**), has been prepared and characterized. It crystallizes in space group $P2_12_12_1$ with $a = 13.739$ (3) Å, $b = 13.774$ (3) Å, $c = 14.211$ (2) Å, $V = 2689$ (2) Å^3, and $Z = 4$. These two compounds together with eight others that have been previously studied structurally are used to examine the relationship between the energy of the $A_{1g} \rightarrow A_{2u}$ (δ → δ*) electronic transition and the strength of the δ bond. The latter is taken to be a linear function of cos (2χ), where χ is the angle of internal rotation away from the fully eclipsed conformation. The observed transition energies extrapolate to a value of (11.8 ± 0.3) × 10^3 cm^{-1} at cos (2χ) = 0. It is proposed that this "residual" energy can be attributed mainly to the difference between the correlation energies in the ground ($\sigma^2\pi^4\delta^2$) and excited ($\sigma^2\pi^4\delta\delta^*$) electron configurations. The extrapolated energy is close to those obtained in previous electronic structure calculations on $Mo_2Cl_8^{4-}$ and related systems.

Introduction

It has been noted[1,2] that the δ components of metal–metal bonds of order 3.5 and higher, especially those of order 4, where the δ-bonding orbital is doubly occupied, have interesting structural and spectroscopic properties. In compounds of the type $M_2X_4(LL)_2$, where LL is a bridging bidentate ligand such as an $R_2P(CH_2)_nPR_2$ type diphosphine, the steric requirements of the LL ligands introduce various angles of internal rotation, χ, away from the angle χ = 0 that defines the precisely eclipsed conformation in which the δ-bond strength has its maximum value. These

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[1] Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982; pp 390–402.

[2] Cotton, F. A. *Chem. Soc. Rev.* **1983**, *12*, 35.

0020-1669/85/1324-0177$01.50/0