J. Am. Chem. Soc. **1988**, *110*, 5761-5764

was treated under argon with refluxing methanol:HCl (10:1, 5 mL) and, after complete solution, the $^{57}FeCl_2$ was isolated by bulb-to-bulb distillation of solvent. A suspension of porphyrin free base (200 mg) in degassed dimethylformamide (30 mL) was added and the mixture refluxed for 24 h under argon. The dimethylformamide was distilled off in vacuo and the solid residue chromatographed over silica with chloroform eluant, yielding a mixture of chloro and hydroxo (porphinato)iron(III) complexes (90 mg). The pure hydroxo complex was obtained by stirring a methylene chloride solution of the mixture overnight with an equal volume of 2 N potassium hydroxide.

Oxidation of the Hydroxo Complex. The tetrahydrofuran and dimethylformamide adducts of the oxoferryl complex were obtained by oxidation at -60 °C in the appropriate solvent with a 4-fold molar excess of *m*-chloroperoxybenzoic acid. The 1-methylimidazole adduct was prepared by addition of a 10-fold molar excess of 1-methylimidazole to the tetrahydrofuran adduct. Solutions for UV-vis spectroscopy were prepared by mixing appropriately diluted stock solutions in a fused silica UV cuvette in a cryostat in the sample compartment of the spectrophotometer. Samples for laser Raman spectra (1.3×10^{-3} M) were prepared by mixing solutions of the porphyrin complex and oxidant in a fused silica cuvette in a low-temperature bath and transferring the cuvette to the sample compartment. Samples for ^{1}H NMR were similarly prepared in an NMR tube and transferred to the spectrometer probe. Mössbauer samples (2.4×10^{-3} M) were generated in the sample holder (10 mm × 12 mm o.d. delrin cup) glued to a glass adaptor with a milled end by low-temperature epoxy resin (Oxford Instruments, M5) and frozen by plunging the apparatus into liquid nitrogen. The delrin cup was cut from the joint under liquid nitrogen and transferred to the spectrometer.

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Registry No. 1, 115227-09-3; **2**, 115227-10-6; **3**, 115227-11-7; **4**, 115227-12-8; **5**, 115244-47-8; mCPBA, 937-14-4; TPP(2,4,6-OCH_3)FeCl, 53470-05-6; DMF(TPP(2,4,6-OCH_3))Fe(O), 115227-13-9; TPP(2,6-Cl)FeOH, 98715-91-4.

Preparation and Molecular and Electronic Structures of a Diamagnetic Diruthenium(II) Compound, $Ru_2[(p\text{-}CH_3C_6H_4)NNN(p\text{-}CH_3C_6H_4)]_4$

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Received January 13, 1988

Abstract: The title compound, $Ru_2[(tol)NNN(tol)]_4$, where tol = p-$CH_3C_6H_4$, has been prepared and characterized by X-ray crystallography, cyclic voltammetry, and several forms of spectroscopy. The compound is diamagnetic (by NMR) and shows one reversible oxidation (in CH_2Cl_2) at +0.28 V vs Ag/AgCl. The structure of the molecule has two notable features: It is strictly eclipsed, and the Ru-Ru distance is 2.417 (2) Å. Both of these structural features, as well as the diamagnetism, lead to the conclusion that the electron configuration is $\sigma^2\pi^4\delta^2\pi^{*4}$. This is in contrast to the occurrence of $\sigma^2\pi^4\delta^2\pi^{*3}\delta^*$ or $\sigma^2\pi^4\delta^2\pi^{*2}\delta^{*2}$ configurations in $Ru_2(O_2CR)_4$ compounds. The large δ^*–π^* gap in the $Ru_2(RNNNR)_4$ type compound in contrast to the small one in the $Ru_2(O_2CR)_4$ compounds is in accord with previous theoretical work. The title compound crystallizes as $Ru_2[(tol)NNN(tol)]_4 \cdot 3C_6H_5CH_3$ in space group $P2_1/c$ with a = 10.539 (2) Å, b = 17.064 (5) Å, c = 19.856 (5) Å, β = 102.30 (2)°, V = 3489 (2) Å^3, and Z = 2.

The electronic structures of diruthenium compounds of the type $Ru_2(LL)_4{}^n$, where LL is a three-atom, uninegative, bridging bidentate ligand (e.g., RCO_2^-, o-$PhNC_5H_3N^-$, o-$OC_5H_4N^-$, or $RCONH^-$) and n = 0, 1+, or 2+, have provided interesting challenges to theorists and experimentalists alike.[1] These species have 12, 11, or 10 electrons (for charges of 0, 1+, or 2+, respectively) to be allocated to the orbitals that arise primarily from overlap of metal d orbitals. These will be the σ, π, and δ bonding orbitals, which probably come in that order of increasing energy (though it does not matter here since they are all going to be filled), and their antibonding counterparts. Since the first eight electrons can be assigned to the $\sigma^2\pi^4\delta^2$ configuration, the problems that arise concern the ordering of the δ^*, π^*, and σ^* orbitals and how they are occupied by the remaining four, three, or two electrons. There is no doubt that the σ^* orbital is always well above the other two, but the relative energies of the δ^* and π^* orbitals are not easily predictable nor necessarily the same in all cases.

Three general possibilities need to be considered, viz., (I) $E(\delta^*) \ll E(\pi^*)$, (II) $E(\delta^*) \approx E(\pi^*)$, and (III) $E(\delta^*) \gg E(\pi^*)$. Measured magnetic susceptibilities are highly pertinent to determining the correct order, but are sometimes inconclusive. For example, the presence of three unpaired electrons in an $Ru_2(O_2CR)_4{}^+$ ion indicates case II, but the presence of two unpaired electrons in an $Ru_2(O_2CR)_4$ compound is compatible with either I or II (though III is ruled out). The interpretation of structural results is generally ambiguous. For $Ru_2(O_2CR)_4{}^{0,1+,2+}$ compounds the Ru-Ru distances vary only over the narrow range 2.248–2.292 Å, but there are also variations in the axial ligands, the effect of which is unknown.

We report here the preparation and properties, including its structure, of $Ru_2[(tol)NNN(tol)]_4$.[2] We shall show that the properties of this compound lead unambiguously to the conclusion that we are dealing with case III, whereby an overall $\sigma^2\pi^4\delta^2\pi^{*4}$ electron configuration is produced.

Experimental Section

Reactions were carried out under anaerobic conditions in standard Schlenkware. Starting materials, $Ru_2(OAc)_4$[3] and di-p-tolyltriazene,[4]

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[1] For background and complete references through 1984, see: (a) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; Wiley: New York, 1982. (b) Cotton, F. A.; Walton, R. A. *Struct. Bonding (Berlin)* **1985**, *62*, 19.

[2] The abbreviation (tol)NNN(tol) is used for the anion $[(p\text{-}CH_3C_6H_4)N{=}N{=}N(p\text{-}(CH_3C_6H_4)]^-$.

[3] Lindsay, A. J.; Wilkinson, G.; Motevalli, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1985**, 2321.

Table I. Crystal Data for $Ru_2(CH_3C_6H_4N_3C_6H_4CH_3)_4$

formula	$Ru_2N_{12}C_{77}H_{80}$
formula wt	1375.72
space gp	$P2_1/c$
syst absences	$0k0$, $k \neq 2n$; $h0l$, $l \neq 2n$
a, Å	10.539 (2)
b, Å	17.064 (5)
c, Å	19.856 (5)
α, deg	90
β, deg	102.30 (2)
γ, deg	90
V, Å^3	3489 (2)
Z	2
d_{calcd}, g/cm^3	1.309
cryst size, mm	0.2 × 0.2 × 0.2
μ(Mo Kα), cm^{-1}	4.731
data colln instrum	Rigaku AFC5R
radiatn (monochrom in incident beam)	Mo Kα (λ_α = 0.71073 Å)
orientation reflcn: no., range (2θ)	25, $14 < 2\theta < 25$
temp, °C	22
scan method	ω
data colln range, 2θ, deg	4, 45
no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	3013, 1504
no. of param refined	351
transmissn factors: max, min	1.0, 0.8789
R^a	0.0679
R_w^b	0.0794
quality of fit indicator^c	1.481
largest shift/esd, final cycle	0.36
largest peak, e/Å^3	0.51

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

were prepared according to the literature. $Ru_2(OAc)_4$ was recrystallized from MeOH and gently warmed under vacuum to remove the solvent.

$Ru_2(CH_3C_6H_4N_3C_6H_4CH_3)_4$. $Ru_2(OAc)_4$, 0.438 g (1 mmol), was suspended in 20 mL of diethyl ether. To this a suspension of 4 mmol of the lithium di-*p*-tolyltriazenido salt in 20 mL of Et_2O was added via cannula (the salt was prepared by neutralizing 0.90 g of di-*p*-tolyltriazene (4 mmol) with 2.67 mL of 1.5 M *n*-BuLi in 20 mL of Et_2O). The reaction mixture was stirred at room temperature for 20 h and then evaporated to dryness, and the solid residue was treated with 20 mL of MeOH and filtered. The precipitate collected on a filter stick was washed repeatedly with MeOH until washings were colorless or pink, not brown. The product was dissolved in hot toluene to give a deep purple solution, which upon cooling to about −15 °C deposited crystalline material. It was filtered and vacuum dried: yield ca. 0.38 g (35%). This crystalline material contains interstitial toluene (as shown by ^1H NMR and X-ray crystallography), which is easily lost. ^1H NMR ($CDCl_3$): δ 2.841 (s, CH_3), 6.914–7.251 (m, aromatic protons). An additional peak at 2.35 ppm due to free toluene was always present in varying amounts depending upon sample drying time. IR (Nujol mull, cm^{-1}): 1605 w, 1580 w, 1505 s, 1467 s, 1380 m, 1315 s, 1290 s, 1220 m, 1180 w, 1118 w, 890 w, 830 s, 800 w, 740 m, 705 w, 680 w, 655 w, 605 m, 540 m, 478 m. UV-vis (CH_2Cl_2 solution nm (M^{-1} cm^{-1}): λ 810 (ϵ 3120); λ 540 (ϵ 13 580); λ 327 (ϵ 63 000).

Measurements. The instruments used were as follows: Cary 17D, UV-vis; Perkin-Elmer 785, IR; Varian XL-200, ^1H NMR; BAS-100, cyclic voltammetry. Cyclic voltammograms were recorded on 0.2 M $(n\text{-}Bu)_4NPF_6$ solutions in CH_2Cl_2 at a Pt electrode, and the reference electrode was Ag/AgCl. Under the experimental conditions ferrocene was oxidized at +0.49 V. The scan speed was 200 mV/s. All solutions used in the NMR and electrochemical measurements were prepared from freshly recrystallized, macrocrystalline material that appeared homogeneous by visual examination under a microscope.

X-ray Crystallography. Single crystals of $Ru_2[(tol)NNN(tol)]_4\cdot 3C_6H_5CH_3$ were grown by layering a toluene solution of the compound with hexane. These crystals lose solvent when exposed to an inert atmosphere. They also react with various glues commonly used for mounting crystals. Finally, after much difficulty because of the fragility of the crystals, a crystal coated with mineral oil was wedged in a Lindemann capillary under argon. Indexing revealed a monoclinic cell, and the axial dimensions and Laue class 2/m were confirmed with oscillation photographs. The data were collected on a Rigaku AFC5R diffractometer with a constant speed of 16°/min. Each scan was repeated three times or until $F/\sigma(F)$ reached 25, whichever came first. The data were collected out to 45° in 2θ. Data were corrected for decay (8.5%), Lorentz and polarization effects,[5] and absorption.[6] An absorption correction was done in two steps: (1) An empirical absorption correction based on selected ψ scans with an Eulerian χ angle near 90° was made. (2) After the structure was solved and refined, the program DIFABS[7] was applied. All non-hydrogen atoms were treated anisotropically, with the exception of C(35) and solvent molecules. One of the toluene molecules resides on a general position and refined well. A second toluene molecule, residing on an inversion center and thus disordered, refined with difficulty, and the methyl group could not be located. Crystallographic and procedural data are presented in Table I, and the atomic positional parameters, in Table II.

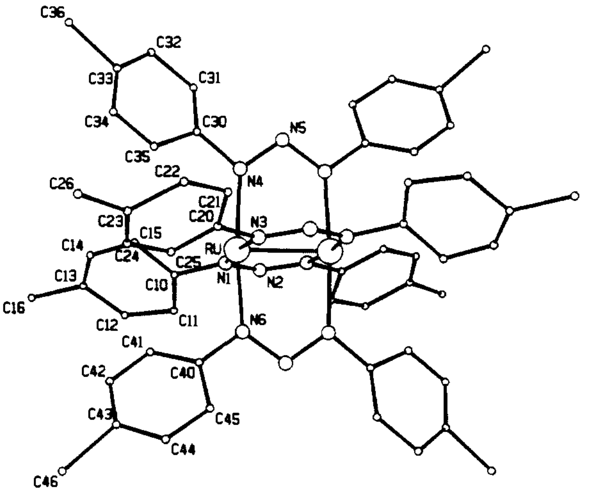

Figure 1. $Ru_2[(tol)NNN(tol)]_4$ molecule, with the atom-numbering scheme.

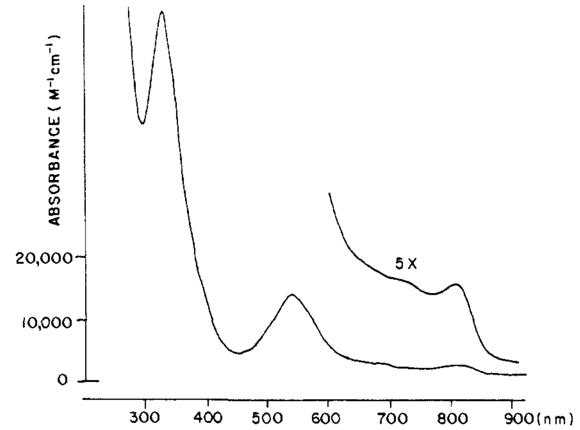

Figure 2. Visible absorption spectrum of $Ru_2[(tol)NNN(tol)]_4$ in CH_2Cl_2 solution.

Results

The compound was prepared as dark purple (virtually black) crystals by the reaction of $Ru_2(OAc)_4$ with Li(tol)NNN(tol) in diethyl ether and recrystallized from toluene. These crystals contained interstitial toluene molecules. X-ray crystallography revealed 3 molecules of toluene/dimer. The presence of toluene was confirmed by ^1H NMR, but the amount varied, depending upon sample drying time. The crystals lost toluene easily upon exposure to a dry atmosphere or vacuum.

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(4) *Organic Syntheses*; Wiley, New York, 1943; Collect. Vol. II, p 163 (the method given here for the preparation of diphenyltriazene was modified as necessary).

(5) Calculations were done on a MicroVaxII, Laboratory for Molecular Structure and Bonding, Texas A&M University, with a SDP-Plus package software.

(6) North, A. C. T.; Philips, D. C.; Matthews, F. S. *Acta. Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 351.

(7) Walker, N.; Stuart, D. *Acta Crystallogr. Sect. A: Found. Crystallogr.* **1983**, *A39*, 158.

Table II. Positional Parameters and Their Estimated Standard Deviations for $Ru_2[(tol)NNN(tol)]_4{\cdot}3C_6H_5CH_3$

atom	*x*	*y*	*z*	*B*,[a] Å^2
Ru	0.0322 (1)	0.0378 (1)	0.45492 (8)	3.84 (3)
N(1)	-0.144 (1)	0.0114 (8)	0.3968 (7)	3.8 (4)
N(2)	-0.237 (1)	-0.0267 (9)	0.4174 (7)	4.8 (4)
N(3)	0.202 (1)	0.0588 (7)	0.5218 (7)	4.2 (4)
N(4)	0.108 (1)	-0.0639 (8)	0.4241 (7)	5.0 (4)
N(5)	0.101 (1)	-0.1324 (9)	0.4528 (7)	4.5 (4)
N(6)	-0.048 (1)	0.1334 (8)	0.4926 (6)	3.6 (4)
C(10)	-0.191 (2)	0.045 (1)	0.3294 (9)	5.1 (5)
C(11)	-0.320 (2)	0.073 (1)	0.311 (1)	5.5 (6)
C(12)	-0.363 (2)	0.107 (1)	0.246 (1)	7.8 (7)
C(13)	-0.279 (2)	0.115 (1)	0.199 (1)	7.2 (7)
C(14)	-0.152 (2)	0.087 (1)	0.219 (1)	7.5 (7)
C(15)	-0.106 (2)	0.049 (1)	0.285 (1)	6.2 (6)
C(16)	-0.323 (2)	0.154 (1)	0.129 (1)	8.8 (8)
C(20)	0.314 (2)	0.104 (1)	0.5054 (8)	4.6 (5)
C(21)	0.441 (1)	0.085 (1)	0.533 (1)	6.0 (6)
C(22)	0.535 (2)	0.128 (1)	0.509 (1)	6.5 (6)
C(23)	0.504 (2)	0.189 (1)	0.4620 (9)	5.4 (6)
C(24)	0.369 (2)	0.204 (1)	0.433 (1)	5.1 (5)
C(25)	0.272 (1)	0.159 (1)	0.456 (1)	5.6 (5)
C(26)	0.608 (2)	0.235 (1)	0.437 (1)	7.6 (6)
C(30)	0.180 (2)	-0.071 (1)	0.3695 (9)	5.1 (5)
C(31)	0.185 (2)	-0.143 (1)	0.3358 (9)	6.2 (6)
C(32)	0.262 (2)	-0.149 (1)	0.285 (1)	7.3 (7)
C(33)	0.327 (2)	-0.083 (1)	0.271 (1)	7.8 (7)
C(34)	0.318 (2)	-0.011 (1)	0.304 (1)	7.8 (7)
C(35)	0.240 (2)	-0.003 (1)	0.3543 (9)	5.7 (5)*
C(36)	0.414 (2)	-0.089 (2)	0.217 (1)	11.0 (8)
C(40)	-0.039 (2)	0.213 (1)	0.4692 (9)	5.2 (5)
C(41)	-0.059 (2)	0.222 (1)	0.3952 (9)	5.7 (6)
C(42)	-0.056 (2)	0.297 (1)	0.369 (1)	6.8 (6)
C(43)	-0.037 (2)	0.360 (1)	0.414 (1)	7.0 (6)
C(44)	-0.021 (2)	0.351 (1)	0.484 (1)	7.5 (6)
C(45)	-0.022 (2)	0.276 (1)	0.5129 (9)	6.4 (6)
C(46)	-0.041 (2)	0.445 (1)	0.385 (1)	8.8 (8)
C(50)	0.217 (3)	0.288 (2)	0.212 (1)	12.4 (9)*
C(51)	0.293 (2)	0.290 (2)	0.164 (1)	10.2 (8)*
C(52)	0.313 (3)	0.222 (2)	0.130 (1)	14 (1)*
C(53)	0.267 (3)	0.151 (2)	0.142 (1)	13 (1)*
C(54)	0.194 (2)	0.154 (2)	0.196 (1)	10.2 (8)*
C(55)	0.168 (2)	0.209 (2)	0.239 (1)	11.1 (8)*
C(56)	0.188 (3)	0.344 (2)	0.254 (1)	14 (1)*
C(60)	0.437 (2)	0.528 (2)	0.532 (1)	14 (1)*
C(61)	0.318 (4)	0.466 (3)	0.476 (2)	21 (2)*
C(62)	0.436 (3)	0.449 (2)	0.450 (2)	19 (1)*

[a] Values denoted by asterisks indicate isotropically refined atoms. Anisotropically refined atoms are given in the form of the equivalent isotropic displacement 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 (Å) and Bond Angles (deg) for $Ru_2[(tol)NNN(tol)]_4{\cdot}3C_6H_5CH_3$[a]

Distances			
Ru-Ru	2.417 (2)	N(1)-N(2)	1.31 (2)
Ru-N(1)	2.02 (1)	N(2)-N(3)	1.30 (2)
Ru-N(3)	2.02 (1)	N(4)-N(5)	1.31 (2)
Ru-N(4)	2.06 (1)	N(5)-N(6)	1.32 (2)
Ru-N(6)	2.05 (1)		
Angles			
Ru-Ru-N(1)	86.3 (4)	N(3)-Ru-N(6)	89.8 (5)
Ru-Ru-N(3)	87.6 (4)	N(4)-Ru-N(6)	174.9 (6)
Ru-Ru-N(4)	87.7 (4)	Ru-N(1)-N(2)	126 (1)
Ru-Ru-N(6)	87.2 (4)	N(1)-N(2)-N(3)	115 (1)
N(1)-Ru-N(3)	173.8 (6)	Ru-N(3)-N(2)	124 (1)
N(1)-Ru-N(4)	90.7 (5)	Ru-N(4)-N(5)	124 (1)
N(1)-Ru-N(6)	89.1 (5)	N(4)-N(5)-N(6)	116 (1)
N(3)-Ru-N(4)	89.8 (5)	Ru-N(6)-N(5)	125 (1)

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

The crystal structure was determined by standard procedures and afforded no special problems except that one of the interstitial toluene molecules was at inversion center and hence disordered. In addition, a toluene molecule was located on a general position and refined well. The molecule is shown in Figure 1, and its principal dimensions are listed in Table III. The molecule lies on an inversion center and is strictly eclipsed, the central portion having effectively D_{4h} symmetry.

The visible spectrum is shown in Figure 2 and is consistent with the purple color of the solution. Very strong charge-transfer absorption rises into the UV. The partially resolved band at ca. 810 nm may be a $\pi^* \rightarrow \sigma^*$ (Ru-N) transition. The compound gives a normal ^{1}H NMR spectrum ($CDCl_3$) with signals at 2.841 (s) and 6.914-7.251 (m) ppm. It is thus clearly diamagnetic. The electrochemical behavior has been examined by cyclic voltammetry with the results shown in Figure 3. It shows two oxidations and one reduction. The solution can be shown to be free of excess ligand by the absence of any feature at +1.1 V where the free ligand has been shown to have a strong, irreversible oxidation wave. The oxidation at +0.28 V is reversible ($I_c = I_a$) and most likely metal based to give a Ru_2^{5+} core. The reduction at -1.13 V is quasi-reversible. When the reduction is carried past this point, new features are observed in the cyclic voltammogram at ca. +0.9 V. The oxidation at +1.48 V is irreversible. The electrochemical behavior of our compound is similar to, but not identical with, that observed for Ru_2(triazene)$_4$ by Wilkinson,[8] who reports two oxidations (+0.16 and +1.28 V) and one reduction (-1.06 V) (these potentials are referenced to SCE). All three couples were reported to be reversible.

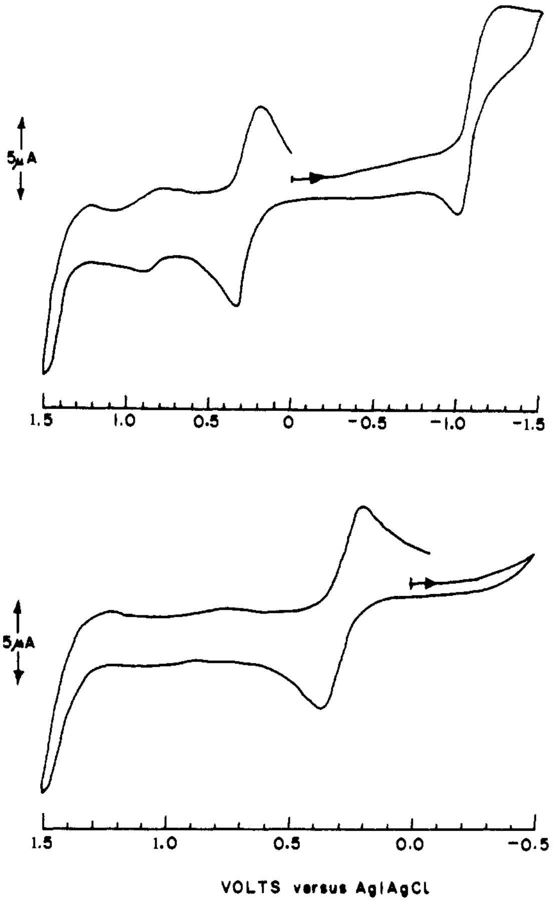

Figure 3. Cyclic voltammograms of $Ru_2[(tol)NNN(tol)]_4$ in CH_2Cl_2 with $(n\text{-}Bu)_4NPF_6$ as supporting electrolyte. Potentials are vs the Ag/AgCl electrode.

Discussion

The diamagnetism of this compound appears to have no other reasonable explanation than the assignment of a $\sigma^2\pi^4\delta^2\pi^{*4}$ configuration, with the δ^* orbital far enough above π^* to be inaccessible thermally at room temperature. The structure supports

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[8] Lindsay, A. J.; Wilkinson, G.; Motevalli, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1987**, 2723.

Table IV. Comparison of Some M–M Distances (Å) and Torsion Angles (deg) in $M_2(RNXNR)_4$ Molecules (R = C_6H_5, p-$CH_3C_6H_4$; X = N, CH, CC_6H_5)

M_2^{4+}	PhNCPhNPh	(tol)NCH-N(tol)	(tol)NNN(tol)	PhNNNPh
Ru_2^{4+}			2.417 (2)[a]	
Rh_2^{4+}	2.389[b]	2.4336 (4)[c]		
	17.3	16.7		
Pd_2^{4+}		2.622 (3)[d]		2.563 (1)[e]
		15		15

[a] This work. [b] Le, J. C.; Chavan, M. Y.; Chau, L. K.; Bear, J. L.; Kadish, K. M. *J. Am. Chem. Soc.* **1985**, *107*, 7195. No esd given. [c] Piraino, P.; Bruno, G.; Lo Schiavo, S.; Laschi, F.; Zanello, P. *Inorg. Chem.* **1987**, *26*, 2205. [d] Cotton, F. A.; Matusz, M.; Poli, R.; Feng, X. *J. Am. Chem. Soc.* **1988**, *110*, 1144. [e] Corbett, M.; Hoskins, B. F.; McLeod, N. J.; O'Day, B. P. *Aust. J. Chem.* **1975**, *28*, 2377.

this conclusion in two ways. The eclipsed configuration indicates that a net δ bond is present. In all comparable structures (see Table IV) where the δ^* orbital must contain two electrons, thus abolishing the δ bond, there are torsion angles of ca. 16°.

The Ru–Ru bond length is also in excellent accord with the $\sigma^2\pi^4\delta^2\pi^{*4}$ configuration. For $Ru_2(O_2CR)_4^+$ species with three unpaired electrons, the configuration must be $\sigma^2\pi^4\delta^2(\pi^*\delta^*)^3$, where we have case II, $E(\pi^*) \approx E(\delta^*)$.[9] In these compounds there are two π^* electrons, and the Ru–Ru distances are about 2.26 Å. The very much larger distance in $Ru_2[(tol)NNN(tol)]_4$, 2.417 (2) Å, is in accord with the addition of another two strongly antibonding π^* electrons. The concomitant loss of one very weakly antibonding δ^* electron is comparatively negligible. Since the $Ru_2(O_2CR)_4L_2$ compounds[3] all have magnetic moments of ca. 2.9 μ_B, indicating two unpaired electrons, they must have either $\delta^{*2}\pi^{*2}$ or $\pi^{*3}\delta^*$ configurations. From the fact that their Ru–Ru distances[4] are virtually the same as those of the $Ru_2(O_2CR)_4^+$ species, the former would seem to be indicated. Finally, as shown in Table IV, when the similarity of the Ru–Ru distance in $Ru_2[(tol)NNN(tol)]_4$ to the Rh–Rh distances in similar Rh_2^{4+} species (where both the π^* and δ^* orbitals must be filled) is taken into consideration, the case for a π^{*4} configuration is supported. It is also seen in Table IV that the further addition of two σ^* electrons (as in the Pd_2^{4+} species) again causes a sizeable increase in the M–M distance.

Our results and conclusions are in excellent accord with the theoretical and photoelectron spectroscopic studies[10] recently reported for $Rh_2[(tol)NCHN(tol)]_4$. This molecule has two more electrons than our $Ru_2[(tol)NNN(tol)]_4$, and the calculation, supported by the measured UV-PES, assigns them to an orbital of b_{1u} symmetry that is primarily a δ^* (Rh–Rh) orbital. This orbital (the HOMO) lies about 8000 cm^{-1} above the π^* orbital. Thus, if we were to deduce the electron configuration of $Ru_2[(tol)NNN(tol)]_4$ from that established for $Rh_2[(tol)NCHN(tol)]_4$ by removing two electrons (which seems an eminently reasonable thing to do), we should arrive at the $\sigma^2\pi^4\delta^2\pi^{*4}$ configuration, which is exactly the one indicated directly by experimental data for $Ru_2[(tol)NNN(tol)]_4$. The similarity of the Ru–Ru and Rh–Rh distances in these two compounds shows that the δ^* orbital is not a major factor in determining M–M bond strength. The major result of losing the two δ^* electrons is the reestablishment of a net δ bond, and this imposes an eclipsed configuration in $Ru_2[(tol)NNN(tol)]_4$ instead of the twisted one (16.7°) found in $Rh_2[(tol)NCHN(tol)]_4$.

Another important result given by the calculations on the rhodium compounds[10] is that the large (ca. 1 eV) separation of the δ^* and π^* orbitals in the $Rh_2(RNCHNR)_4$ type compound is in sharp contrast to the small (<0.1 eV) difference in $Rh_2(O_2CH)_4$. Again when the Rh_2^{4+} compound minus two electrons is used as a model for the corresponding Ru_2^{4+} compound, it is clear that for $Ru_2(O_2CR)_4$ compounds the presence of two unpaired electrons is to be expected. We note once again that the large decrease in the Ru–Ru distance on going from $Ru_2[(tol)NNN(tol)]_4$ to $Ru_2(O_2CR)_4L_2$ compounds, viz., 2.42–2.26 = 0.16 Å, leads us to prefer a $\delta^{*2}\pi^{*2}$ configuration rather than a $\pi^{*3}\delta^*$ configuration for the carboxylates.

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Supplementary Material Available: Full listings of bond distances, bond angles, and anisotropic displacement parameters (B's) (4 pages); table of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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An Unusually Facile Formation of Substituted 1,2-Dihydropyridine Derivatives: The Reversible Condensation of Pyridines with Reactive Carbonyl Groups

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Abstract: Temperature-variable spectroscopic examination (^1H and ^{13}C NMR and IR) of the reaction of pyridine with a number of acid halides and anhydrides indicates the reversible formation of novel 2-pyridinyl-1,2-dihydropyridine structures (**1**). The structure results from a nucleophilic attack at the ortho position of the transient 1:1 pyridinium adduct. The reaction is observed to be general for 3- and 4-substituted pyridines. The formation of structures analogous to **1** are favored by electron-withdrawing groups substituted on either the pyridine or carbonyl. Electron-donating substituents favor the production of the simple 1:1 pyridinium salts. The 3-substituted pyridines produce the corresponding 6-addition product (2:1 pyridine–carbonyl).

Interest in a fundamental understanding of the interrelationship of pyridinium–dihydropyridine chemistry continues to be an area of considerable experimental and theoretical effort.[1] Such activity is particularly acute in research directed toward the study of

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