Notes

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A Very Short Ruthenium(II)–Nitrogen Heterocycle Bond: Crystal Structures of Pentaammine(*N*-methylpyrazinium)ruthenium(II) Iodide and Pentaammine(*N*-methylpyrazinium)ruthenium(III) *p*-Toluenesulfonate Pentahydrate

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Received July 23, 1985

Pentaammineruthenium(II) has a very high affinity for π-acid ligands.[1] One of the strongest π-acids among the set of N-heterocycle ligands is the methylpyrazinium (Mepz$^+$) cation. The strong stabilization by the ligand of Ru(II) relative to Ru(III) is shown by the value of $E_{1/2}$ for the $[(NH_3)_5RuMepz]^{4+/3+}$ couple, +0.87 V, compared to that of the $[(NH_3)_5Ru(pz)]^{3+/2+}$ couple (pz = pyrazine), +0.49 V, both vs. NHE.[2,3] The enthalpy of substitution onto $[(NH_3)_5RuOH_2]^{2+}$ is -18.0 ± 0.3 kcal mol^{-1} for Mepz$^+$ and -16.8 ± 0.1 kcal mol^{-1} for pyrazine.[4] The $[(NH_3)_5RuMepz]^{3+}$ complex exhibits two well-resolved metal-to-ligand charge-transfer bands, a feature not at all prominent for $[(NH_3)_5Ru(pz)]^{2+}$. The difference in energy between the two bands has been taken to measure the splitting of the πd levels in the former case.[5] While this interpretation is probably correct to first order, it neglects the effects of excited-state spin–orbit coupling and splitting of nonbonding orbitals due to lowered symmetry.

The structures of $[(NH_3)_5Ru(pz)]^{2+}$ (Ia) and $[(NH_3)_5Ru(pz)]^{3+}$ (Ib) being known,[6] we were interested to learn how the differences between pyrazine and *N*-methylpyrazinium are reflected in the structures of their respective Ru(II) and Ru(III) complexes and undertook to determine the structures of compounds containing the latter ligand.

Experimental Section

Preparation of Pentaammine(*N*-methylpyrazinium)ruthenium(II) Iodide (II). Fifty milligrams of $[(NH_3)_5RuMepz](ClO_4)_3$, prepared by a literature method,[2] was dissolved in 5 mL of 0.2 M NaI solution. Dark purple crystals were deposited by slow evaporation of the solution.

Preparation of Pentaammine(*N*-methylpyrazinium)ruthenium(III) *p*-Toluenesulfonate Pentahydrate (III). Crystals of this compound were prepared by dissolving 20 mg of $[(NH_3)_5RuMepz](ClO_4)_3$ in 1 mL of H_2O. Two drops of 1 M CF_3SO_3H and ten drops of 30% hydrogen peroxide were added by pipet, followed by 2 mL of saturated *p*-toluenesulfonic acid. The oxidation of Ru(III) is slow, but on leaving the solution, initially purple, overnight in the refrigerator, the color changed to yellow and a small quantity of golden crystals was recovered by filtration.

X-ray Crystallography. Data for both structures were collected on a Philips DW1100 four-circle diffractometer. Mo Kα (λ = 0.71069 Å) radiation with a graphite-crystal monochromator in the incident beam was used. The unit cell dimensions were obtained by least-squares fits of 25 reflections in the range $12° < \theta < 15°$ for II and $12° < \theta < 16°$ for III. Data were measured by using an ω–2θ motion. The scan width, $\Delta\omega$, for each reflection was 1° with scan time of 20 s. Background measurements were made for anther 20 s at both limits of each scan. Three standard reflections were monitored every 50 min. No systematic variations in intensities were found. Crystallographic data and other pertinent information are given in Table I. Lorentz and polarization corrections were applied. In the case of II, several ψ-scans showed variations smaller than 5%; therefore, no absorption correction was applied. Due to the small absorption coefficient, intensity data for structure III also were not corrected for absorption.

Table I. Crystallographic Data for $[(NH_3)_5Ru(NC_4H_4NCH_3)]I_3$ (II) and $[(NH_3)_5Ru(NC_4H_4NCH_3)](CH_3C_6H_4SO_3)_4 \cdot 5H_2O$ (III)

	II	III
formula	$C_5H_{22}N_7I_3Ru$	$C_{33}H_{44}N_7O_{17}S_4Ru$
fw	662.06	1040.07
space group	*Pnma*	$P\bar{1}$
a, Å	10.655 (2)	14.298 (2)
b, Å	7.704 (1)	14.668 (2)
c, Å	21.488 (3)	13.551 (2)
α, deg	90	89.94 (3)
β, deg	90	113.21 (4)
γ, deg	90	66.77 (3)
V, Å^3	1764 (1)	2359 (1)
Z	4	2
d(calcd), g cm^{-3}	2.498	1.464
d(exptl), g cm^{-3}	2.45	
cryst size, mm	0.1 × 0.1 × 0.12	0.1 × 0.15 × 0.4
μ, cm^{-1}	57.2	5.11
range of 2θ, deg	3–52	3–45
range of indices	$+h,+k,+l$	$\pm h,\pm k,+l$
no. of unique data	1828	6052
data with $F_o^2 > 3\sigma(F_o^2)$	1344	4220
R	0.041	0.078
R_w	0.053	0.083
w	$(\sigma_F^2 + 0.000994F^2)^{-1}$	σ_F^{-2}
largest peak in difference Fourier, e Å^{-3}	1.2	0.5

Table II. Positional Parameters and Estimated Standard Deviations for $[(NH_3)_5RuMepz]I_3$[a]

atom	*x*	*y*	*z*
I(1)	0.21183 (9)	0.25000 (0)	0.53807 (5)
I(2)	0.3379 (1)	0.25000 (0)	0.35134 (5)
I(3)	0.4270 (1)	0.25000 (0)	−0.22900 (5)
Ru	0.4010 (1)	0.25000 (0)	0.13710 (5)
N(1)	0.5191 (7)	0.444 (1)	0.0988 (3)
N(2)	0.290 (1)	0.25000 (0)	0.0647 (5)
N(3)	0.2945 (8)	0.051 (1)	0.1816 (4)
N(4)	0.527 (1)	0.25000 (0)	0.2165 (5)
N(5)	0.139 (1)	0.25000 (0)	−0.0446 (6)
C(1)	0.162 (1)	0.25000 (0)	0.0671 (7)
C(2)	0.086 (1)	0.2500 (0)	0.0144 (7)
C(3)	0.267 (1)	0.25000 (0)	−0.0487 (7)
C(4)	0.342 (1)	0.25000 (0)	0.0042 (6)
C(5)	0.060 (1)	0.25000 (0)	−0.1015 (7)

[a] Estimated standard deviations in the least significant digits are shown in parentheses.

For compound II, the heavy-atom positions were obtained by using the results of MULTAN direct-method analysis.[7] The structure was refined[8]

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(1) Shepherd, R. E.; Taube, H. *Inorg. Chem.* **1973**, *12*, 1392.
(2) Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1973**, *95*, 1086.
(3) Lim, H. S.; Barclay, D. J.; Anson, F. C. *Inorg.* Chem. **1972**, *11*, 1460.
(4) Wishart, J. F.; Taube, H.; Breslauer, K. J.; Isied, S. S. *Inorg. Chem.* **1984**, *23*, 2997.
(5) Magnuson, R. H.; Taube, H. *J. Am. Chem. Soc.* **1975**, *97*, 5129.
(6) Gress, M. E.; Creutz, C.; Quicksall, C. O. *Inorg. Chem.* **1981**, *20*, 1522.
(7) Main, P.; Hull, S. E.; Lessinger, L.; Germain, G.; Declereq, J. P.; Woolfson, M. M. "MULTAN 78, A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data", Universities of York, England, and Louvain, Belgium, 1978.
(8) All crystallographic computing was done on a CYBER 74 computer at the Hebrew University of Jerusalem using the SHELX-77 structure determination package. Values of the atomic scattering factors and the anomalous terms were taken from: (a) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV. (b) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

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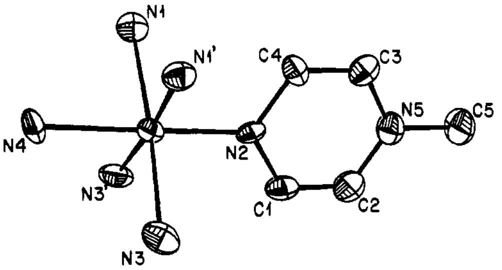

Figure 1. Atomic numbering scheme for $[(NH_3)_5RuMepz]^{3+}$ in structure II.

Table III. Bond Distances and Angles for $[(NH_3)_5RuMepz]I_3$

	Bond Distances, Å		
Ru–N(1)	2.122 (7)	N(5)–C(2)	1.38 (2)
–N(2)(Mepz)	1.95 (1)	–C(3)	1.36 (1)
–N(3)	2.136 (8)	–C(5)	1.49 (2)
–N(4)(trans)	2.17 (1)	C(1)–C(2)	1.39 (2)
N(2)–C(1)	1.37 (1)	C(3)–C(4)	1.39 (2)
–C(4)	1.41 (1)		
	Bond Angles, deg		
N(1)–Ru–N(1)′	89.7 (3)	N(3)–Ru–N(3)′	92.0 (3)
–N(2)	92.8 (3)	–N(4)	88.6 (3)
–N(3)	175.0 (3)	N(3)′–Ru–N(4)	88.6 (3)
–N(3)′	88.9 (3)	Ru–N(2)–C(1)	125.0 (9)
–N(4)	86.5 (3)	–C(4)	119.8 (9)
N(1)–Ru–N(2)	92.8 (3)	C(1)–N(2)–C(4)	115 (1)
–N(3)	88.9 (3)	C(2)–N(5)–C(3)	118 (1)
–N(3)′	175.0 (3)	–C(5)	122 (1)
–N(4)	86.5 (3)	C(3)–N(5)–C(5)	121 (1)
N(2)–Ru–N(3)	92.1 (3)	N(2)–C(1)–C(2)	123 (1)
–N(3)′	92.1 (3)	N(5)–C(2)–C(1)	121 (1)
–N(4)	179.0 (4)	–C(3)–C(4)	122 (1)
		N(2)–C(4)–C(3)	122 (1)

in space group *Pnma* to convergence by using anisotropic thermal parameters for all non-hydrogen atoms. The space group *Pnma* was chosen over the acentric group *Pna*2, because the statistics indicated a centric space group. In the case of compound III, the heavy-atom positions were obtained from a three-dimensional Patterson function. The structure was refined[1a] in the space group *P*1 to convergence by using anisotropic thermal parameters for the ruthenium and sulfur atoms and for the nitrogen atoms in the first coordination sphere. The rest of the non-hydrogen atoms were refined by using isotropic thermal parameters. For both structures, hydrogen atoms were omitted. The final discrepancy indices, $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ are listed in Table I. Lists of all observed and calculated structure factors and of thermal parameters for both structures and tables of bond distances and angles for the anions in compound III are available as supplementary material.

Results

$[(NH_3)_5RuMepz]I_3$ (II). The positional parameters and estimated standard deviations for $[(NH_3)_5RuMepz]I_3$ are given in Table II. Figure 1 shows the pseudooctahedral geometry of the complex. Table III lists the bond distances and angles. The Ru–N(Mepz) distance is 1.95 (1) Å, the shortest yet reported for a ligand of this type.

There are four $[(NH_3)_5RuMepz]^{3+}$ cations and twelve iodides per unit cell. All the cations and anions are located on mirror planes at $y = 0.25$ and $y = 0.75$. The pyrazine ring of the $[(NH_3)_5RuMepz]^{3+}$ ion lies flat on the mirror plane, which also includes atoms N(4), Ru, and C(5).[9] The ruthenium atom deviates from the plane defined by N(1), N(1)′, N(3), and N(3)′ by 0.09 Å in the direction of the methylpyrazinium ligand. The four Ru–Mepz vectors per cell, as defined by the Ru–N(2) bonds, form two antiparallel pairs perpendicular to the *b* axis, with angles between the pairs of 74.6 and 105.4°. The plane defined by atoms N(1), N(2), N(3), and N(4) forms an angle of 89.04° with its mirror image (N(1)′, N(2), N(3)′, and N(4)) and 45.48° with the mirror plane.

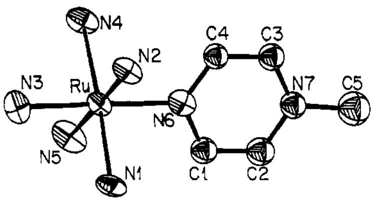

Figure 2. Atomic numbering scheme for $[(NH_3)_5RuMepz]^{4+}$ in structure III.

The geometry of the $[(NH_3)_5RuMepz]^{3+}$ ion is very similar to that previously reported[6] for $[(NH_3)_5Ru(pz)]^{2+}$ (Ia) and $[(NH_3)_5Ru(pz)]^{3+}$ (Ib). Crystal symmetry imposes planarity on the (trans ammine)–ruthenium–pyrazine–(methyl group) framework. The plane of the pyrazine thus bisects the angles between the cis ammines. This staggered conformation is commonly gound in N-heterocycle complexes of ruthenium and osmium ammines.[6,10–13] The structure of the pyrazine is unremarkable, with bonds and angles similar to those found in ref 6. There is no significant difference between the aromatic C–C and C–N bond lengths.

The cis ammines, N(1), N(1)′, N(3), and N(3)′, are pushed slightly away from the methylpyrazinium ligand, forming angles of 92.8 (3) (N(1)–Ru–N(2)) and 92.1 (3)° (N(3)–Ru–N(2)). The angles between the trans and cis ammines are correspondingly compressed to 86.5 (3) (N(1)–Ru–N(4)) and 88.6 (3)° (N(3)–Ru–N(4)).

The Ru–N (ammine) bond lengths are 2.122 (7) and 2.136 (8) Å for the cis ammines and 2.17 (1) Å for the trans ammine. The 0.04 (1) Å difference between the cis and trans distances is evidence for a trans influence, signifying that the trans NH_3–Ru bond is weaker than the cis bonds. Similar effects have been measured in the structures of $[(NH_3)_5RuNO_2]^+$ (cis 2.131 (5) and 2.123 (5) Å; trans 2.199 (6) Å),[14] *cis*-$[(NH_3)_4Ru(isonicotinamide)_2]^{2+}$ (axial 2.143(5) Å; trans 2.170 (6) Å),[15] and $[(NH_3)_5RuMe_2SO]^{2+}$ (cis 2.169 (5) Å (average); trans 2.209 (8) Å).[16] There is no significant difference between the trans (2.166 (7) Å) and cis (average 2.152 (6) Å) Ru–NH_3 distances in $[(NH_3)_5Ru(pz)]^{2+}$.[6]

$[(NH_3)_5RuMepz](CH_3C_6H_4SO_3)_4\cdot 5H_2O$ (III). Positional parameters and estimated standard deviations for III are given in Table IV, and selected bond distances and angles are listed in Table V. The structure of the cation is depicted in Figure 2. Bond distances and angles for the anions are available as supplementary material.

There are two formula units per unit cell. One of the lattice water molecules, corresponding to oxygen atom OW(5), was found to be disordered and was refined in two positions, OW(5) and OW(5)′, each with a half-occupancy factor. A network of hydrogen bonds exists in the crystal lattice among the nitrogen atoms of the coordinated ammines, the water molecules, and the oxygen atoms of the *p*-toluenesulfonate anions. All O–O and N–O

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(9) The least-squares planes for compound II are defined as follows. Plane 1: N(2), C(1), C(2), N(5), C(3), C(4), C(5); $y - 0.25 = 0$. Plane 2: N(1), N(1)′, N(3), N(3)′, $6.357x + 17.24z - 5.004 = 0$. Plane 3: N(1), N(2), N(3), N(4); $6.012x - 5.402y - 9.365z + 0.207 = 0$. Plane 4: N(1)′, N(2), N(3)′, N(4); $6.012x + 5.402y - 9.365z - 2.494 = 0$. The ruthenium atom deviates from planes 1–4 by 0, –0.0903, –0.0165, and –0.0165 Å, respectively.

(10) (a) Fürholz, U.; Bürgi, H.-B; Wagner, F. E.; Stebler, A.; Ammeter, J. H.; Krausz, E.; Clark, R. J. H.; Stead, M. J; Ludi, A. *J. Am. Chem. Soc.* **1984**, *106*, 121. (b) Furholz, U.; Joss, S.; Bürgi, H.-B.; Ludi, A. *Inorg. Chem.* **1985**, *24*, 943.

(11) Sundberg, R. J.; Bryan, R. F.; Taylor, I. F.; Taube, H. *J. Am. Chem. Soc.* **1974**, *96*, 381.

(12) (a) Krentzien, H. J.; Clarke, M. J.; Taube, H. *Bioinorg. Chem.* **1975**, *4*, 143. (b) Kastner, M. E.; Coffey, K. F.; Clarke, M. J.; Edmonds, S. E.; Eriks, K. *J. Am. Chem. Soc.* **1981**, *103*, 5747.

(13) Bino, A.; Lay, P. A.; Taube, H.; Wishart, J. F. *Inorg. Chem.* **1985**, *24*, 3969.

(14) Bottomley, F. *J. Chem. Soc., Dalton Trans.* **1972**, 2148.

(15) Richardson, D. E.; Walker, D. D.; Sutton, J. E.; Hodgson, K. O.; Taube, H. *Inorg. Chem.* **1979**, *18*, 2216.

(16) March, F. C.; Ferguson, G. *Can. J. Chem.* **1971**, *49*, 3590.

Table IV. Positional Parameters and Estimated Standard Deviations for $[(NH_3)_5RuMepz](tos)_4{\cdot}5H_2O$[a]

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Ru	0.71837 (8)	0.49104 (7)	0.78378 (8)	C(17)	0.447 (1)	0.038 (1)	0.130 (1)
N(1)	0.8096 (8)	0.3336 (7)	0.8446 (8)	C(18)	0.445 (1)	0.135 (1)	0.118 (1)
N(2)	0.6853 (8)	0.4588 (7)	0.6253 (7)	C(19)	0.542 (1)	−0.153 (1)	0.158 (1)
N(3)	0.8692 (8)	0.4918 (7)	0.7965 (8)	S(3)	0.9525 (3)	0.2743 (2)	0.6130 (3)
N(4)	0.6350 (8)	0.6481 (7)	0.7231 (8)	O(7)	1.0550 (8)	0.2798 (7)	0.6196 (8)
N(5)	0.7532 (9)	0.5247 (8)	0.9421 (7)	O(8)	0.9301 (7)	0.3090 (7)	0.7049 (7)
N(6)	0.5708 (8)	0.4851 (7)	0.7705 (7)	O(9)	0.8562 (9)	0.3260 (8)	0.5106 (9)
C(1)	0.574 (1)	0.4280 (9)	0.853 (1)	C(20)	0.9773 (9)	0.1475 (9)	0.6262 (9)
C(2)	0.476 (1)	0.419 (1)	0.841 (1)	C(21)	0.898 (1)	0.120 (1)	0.635 (1)
N(7)	0.3792 (8)	0.4657 (7)	0.7487 (8)	C(22)	0.918 (1)	0.017 (1)	0.648 (1)
C(3)	0.374 (1)	0.5250 (9)	0.6692 (9)	C(23)	1.017 (1)	−0.054 (1)	0.652 (1)
C(4)	0.471 (1)	0.5337 (9)	0.6809 (9)	C(24)	1.095 (1)	−0.028 (1)	0.642 (1)
C(5)	0.278 (1)	0.449 (1)	0.736 (1)	C(25)	1.079 (1)	0.072 (1)	0.629 (1)
S(1)	0.5559 (3)	0.2733 (2)	0.6047 (2)	C(26)	1.038 (1)	−0.167 (1)	0.668 (1)
O(1)	0.6563 (8)	0.2657 (7)	0.6973 (8)	S(4)	0.1050 (3)	0.2972 (2)	0.0757 (3)
O(2)	0.4640 (7)	0.2886 (7)	0.6333 (7)	O(10)	0.1630 (9)	0.2922 (8)	0.1889 (9)
O(3)	0.5226 (7)	0.3496 (6)	0.5133 (7)	O(11)	−0.011 (1)	0.3599 (8)	0.0300 (9)
C(6)	0.5923 (9)	0.1557 (8)	0.5620 (9)	O(12)	0.157 (1)	0.330 (1)	0.016 (1)
C(7)	0.615 (1)	0.1450 (9)	0.470 (1)	C(27)	0.1215 (9)	0.1753 (9)	0.0523 (9)
C(8)	0.648 (1)	0.049 (1)	0.442 (1)	C(28)	0.105 (1)	0.1539 (9)	−0.052 (1)
C(9)	0.660 (1)	−0.034 (1)	0.504 (1)	C(29)	0.116 (1)	0.0571 (9)	−0.071 (1)
C(10)	0.634 (1)	−0.020 (1)	0.590 (1)	C(30)	0.145 (1)	−0.0169 (9)	0.013 (1)
C(11)	0.602 (1)	0.075 (1)	0.623 (1)	C(31)	0.161 (1)	0.006 (1)	0.115 (1)
C(12)	0.703 (1)	−0.138 (1)	0.474 (1)	C(32)	0.149 (1)	0.102 (1)	0.137 (1)
S(2)	0.5459 (3)	0.2596 (3)	0.1200 (3)	C(33)	0.157 (1)	−0.122 (1)	−0.008 (1)
O(4)	0.4391 (8)	0.3281 (7)	0.0332 (8)	OW(1)	1.0553 (9)	0.4089 (8)	0.4715 (9)
O(5)	0.5595 (8)	0.2858 (7)	0.2262 (7)	OW(2)	0.249 (1)	0.3994 (9)	0.4527 (9)
O(6)	0.6384 (9)	0.2486 (8)	0.0939 (9)	OW(3)	0.957 (1)	0.3956 (9)	1.247 (1)
C(13)	0.543 (1)	0.1410 (9)	0.127 (1)	OW(4)	0.867 (1)	0.619 (1)	1.196 (1)
C(14)	0.641 (1)	0.053 (1)	0.145 (1)	OW(5)	0.794 (1)	0.351 (1)	0.092 (1)
C(15)	0.637 (1)	−0.041 (1)	0.155 (1)	OW(5)′	0.724 (1)	0.384 (1)	0.109 (1)
C(16)	0.540 (1)	−0.046 (1)	0.149 (1)				

[a] Estimated standard deviations in the least significant digits are shown in parentheses.

Table V. Major Bond Distances and Angles for $[(NH_3)_5RuMepz](tos)_4{\cdot}5H_2O$

	Bond Distances, Å		
Ru–N(1)	2.118 (8)	N(6)–C(1)	1.37 (1)
–N(2)	2.107 (9)	–C(4)	1.36 (1)
–N(3)(trans)	2.10 (1)	N(7)–C(2)	1.35 (1)
–N(4)	2.112 (9)	–C(3)	1.34 (1)
–N(5)	2.109 (9)	–C(5)	1.51 (2)
–N(6)(Mepz)	2.08 (1)	C(1)–C(2)	1.41 (2)
		C(3)–C(4)	1.39 (2)
	Bond Angles, deg		
N(1)–Ru–N(2)	88.0 (5)	N(4)–Ru–N(5)	87.8 (5)
–N(3)	87.6 (5)	–N(6)	92.4 (5)
–N(4)	177.0 (4)	N(5)–Ru–N(6)	91.2 (4)
–N(5)	92.5 (5)	Ru–N(6)–C(1)	120 (1)
–N(6)	90.6 (5)	–C(4)	122.2 (7)
N(2)–Ru–N(3)	89.2 (4)	C(1)–N(6)–C(4)	118 (1)
–N(4)	91.7 (5)	C(2)–N(7)–C(3)	121 (1)
–N(5)	178.9 (4)	–C(5)	119 (1)
–N(6)	89.8 (4)	C(3)–N(7)–C(5)	120 (2)
N(3)–Ru–N(4)	89.4 (5)	N(6)–C(1)–C(2)	120 (2)
–N(5)	89.8 (5)	N(7)–C(2)–C(1)	120 (1)
–N(6)	178.0 (5)	–C(3)–C(4)	119 (2)
		N(6)–C(4)–C(3)	122 (1)

distances lie in the normal ranges for hydrogen bonds of 2.65–2.85 and 2.85–2.95 Å, respectively.

The $[(NH_3)_5RuMepz]^{4+}$ cation has the typical configuration, with the pyrazinium ring staggered between the cis ammines. The plane of the ring forms dihedral angles of 43.4° with the plane defined by N(1), N(3), N(4), and N(6) and 49.0° with the plane defined by N(2), N(3), N(5), and N(6).[17] The cis ammines, N(1), N(2), N(4), and N(5), form N–M–N angles of 90.6 (5), 89.8 (5), 94.2 (5), and 91.2 (4)°, respectively, with the methylpyrazinium ligand.

The Ru(III)–N(ammine) bond lengths average 2.11 Å, typical of ruthenium(III) ammine complexes.[6] The trans bond distance (2.10 (1) Å) is not significantly different from the cis distances, as opposed to the ruthenium(II) case. The ruthenium(III)–methylpyrazinium bond length is 2.08 (1) Å, the same as was observed for the ruthenium(III)–pyrazine distance in $[(NH_3)_5Ru(pz)](CF_3SO_3)_3.H_2O$.[6]

The C–C bonds in the methylpyrazinium ligand are longer (1.39 (2) and 1.41 (2) Å) than the C–N bonds (1.34 (1), 1.35 (1), 1.36 (1), and 1.37 (1) Å), as observed previously in the structure of free pyrazine.[18] Such differences were not observed in compounds Ia, Ib, and II.

Discussion

The strength of the ruthenium(II)–methylpyrazinium bond is indicated by the very short Ru–N(2) distance of 1.95 (1) Å. By way of comparison, the Ru–N(pz) distance[6] is 2.006 (6) Å in $[(NH_3)_5Ru(pz)]^{2+}$ and the Ru–N(isn) distances[15] in *cis*-$[(NH_3)_4Ru(isn)_2]^{2+}$ are 2.044 (6) and 2.072 (5) Å. The shortest Ru–N(heterocycle) distance previously reported was found by Clarke et al.[19] in the complex $[(NH_3)_4Ru(10\text{-methylisoalloxazine})]^{2+}$. The bond length of 1.980 (6) Å is short due to a strong back-bonding interaction, as evidenced by distortion signifying partial reduction of the planar isoalloxazine. Similar evidence of partial reduction of *N*-methylpyrazinium in $[(NH_3)_5RuMepz]^{3+}$ is uncertain, since the site symmetry forces the ligand to be planar. The thermal parameters of atoms N(5) and C(5) (see Figure 1) seem to indicate a possibility of some out-of-plane bending due to reduction, but it would have to be small.

The Ru–N distance of 1.95 (1) Å that we report is not the shortest Ru(II)–N distance known. Dinitrogen, nitrosyl, and nitro

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[17] The least-squares planes in compound III are defined as follows. Plane 1: N(1), N(3), N(4), N(6); $-1.2050x + 4.2260y + 12.676z - 11.134 = 0$. Plane 2: N(2), N(3), N(5), N(6); $0.049684x - 12.417y + 2.5709z + 4.0345 = 0$. Plane 3: N(6), C(1), C(2), N(7), C(3), C(4); $2.0229x - 11.190y - 8.0934z + 10.523 = 0$. The ruthenium atom deviates from planes 1–3 by 0.0107, −0.0112, and 0.1385 Å, respectively. Atom C(5) deviates 0.0971 Å from plane 3.

[18] Wheatley, P. *J. Acta Crystallogr.* **1957**, *10*, 182.

[19] Clarke, M. J.; Dowling, M. G.; Garafalo, A. R.; Brennan, T. F. *J. Am. Chem. Soc.* **1979**, *101*, 223.

ligands form bonds with Ru(II) that are shorter than the distance found in $[(NH_3)_5RuMepz]^{3+}$. In $[(NH_3)_5Ru)_2N_2](BF_4)_4$, the Ru-N(dinitrogen) bond length is 1.928 (6) Å.[20] The Ru-N-(nitrosyl) distance in $[(NH_3)_5RuNO]Cl_3\cdot H_2O$ is 1.770 (9) Å.[21] The Ru-N(nitro) distance in $[(NH_3)_5RuNO_2]Cl\cdot H_2O$ is 1.906 (5) Å.[14]

The shrinking of the Ru-N(Mepz) bond when Ru(III) is reduced has implications for the reactivity of the couple as a redox reagent, and it is of interest to estimate the magnitude of the effect. A major cause of the difference in the self-exchange rates for the $Fe(H_2O)^{3+/2+}$ and $Ru(NH_3)^{3+/2+}$ couples is the difference in the inner-sphere reorganization energies, estimated by Sutin[22] as 8.4 kcal/mol for the former couple and 0.9 for the latter. In this connection it is of interest to learn what the effect of the shortening of the Ru-N(Mepz) bond on reducing Ru(III) to Ru(II) on the self-exchange rate is expected to be. Calculations using for the present case $\Delta r = -0.13$ and 0.03 Å for the Ru-N(Mepz) and $Ru-N(NH_3)$ bonds, respectively, on reduction and the assumption made by Sutin for the force constants yielded an inner-sphere reorganization energy of 1.6 kcal. In view of the difference in charge type (4+/3+ in the present case compared to 3+/2+), it would be difficult to trace the effect on this particular structural parameter on the rates of electron transfer for the couple.

Acknowledgment. Support of this work by a National Science Foundation Graduate Fellowship for J.F.W. is gratefully acknowledged.

Registry No. II, 103026-88-6; III, 103026-90-0; $[(NH_3)_5RuMepz](ClO_4)_3$, 41557-35-1.

Supplementary Material Available: Listings of thermal parameters for both structures and tables of bond distances and angles for the anions in compound III (6 pages). Ordering information is given on any current masthead page.

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(20) Treitel, I. M.; Flood, M. T.; Marsh, R. E.; Gray, H. B. *J. Am. Chem. Soc.* **1969**, *91*, 6512.

(21) Bottomley, F. *J. Chem. Soc., Dalton Trans.* **1974**, 1600.

(22) Sutin, N. In *Tunneling in Biological Systems*; Chance, B., DeVault, D. C., Frauenfelder, H.; Marcus, R. A., Schrieffer, J. R., Sutin, N., Eds.; Academic: New York, 1979; pp 201-227.

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Molecular Orbital Calculations Relevant to the Hyper-Closo vs. Iso-Closo Controversy in Metallaboranes

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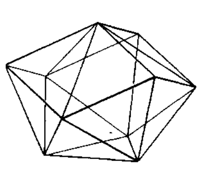
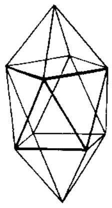
Received April 25, 1986

Greenwood, Kennedy and their co-workers[1] have recently described some interesting metallaboranes whose polyhedral structures are not those normally found for nine- and ten-vertex *closo*-metallaboranes. An example of such a ten-vertex metallaborane is illustrated in **1** and contrasted with the more usual bicapped square-antiprismatic geometry (**2**).[2] Since both **1** and **2** have triangular faces exclusively, Greenwood et al. have suggested that **1** is an isomeric form of **2** and recommended that it and related structures be described as iso-closo-.[3,4] Baker[5] has noted that if the metal fragment in **1** contributes its usual number of electrons for skeletal bonding then **1** has one fewer skeletal electron pairs than **2** and suggested that **1** represents an example of a new class of hyper-closo polyhedra with *n* rather than *n* + 1 skeletal electron pairs. Baker[5] has proposed that the capping principle[6] can be adapted to account for the electron deficiency in **1**, although, as Kennedy has noted,[7] **1** is geometrically quite distinct from the capped closo structure **3** anticipated from the capping rules. Kennedy has surmised that if the metal contributes four orbitals to skeletal bonding rather than the three generally assumed in simple electron-counting rules,[8] then it is not unreasonable for high-connectivity clusters such as **1** to be expected.



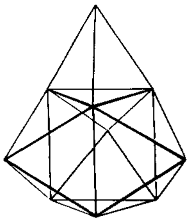
1

e.g. $[H(PPh_3)(Ph_2PC_6H_4Ir(B_9H_8)]$



2

e.g. $[RhH(PEt_3)_2(C_2B_9H_7)]$



3

In this paper we now describe some molecular orbital calculations and a theoretical analysis based on Stone's tensor surface harmonic theory[9-11] that resolve this controversy.

In Table I the computed total energies for $B_{10}H_{10}$ and the metallaborane $B_9H_9M(CO)_3$[12] are presented for idealized geometries based on **1**-**3** and electron counts corresponding to the presence of 10 and 11 skeletal electron pairs. Even for the boranes the calculations provide a clear geometric distinction: the bicapped square-antiprismatic geometry (**2**) is the favored geometry for *n* + 1 skeletal electron pairs, and **1** is favored for *n* skeletal electron pairs. The tetracapped trigonal prism (**3**) is also characterized by *n* bonding skeletal electron pairs, in accordance with the capping principle;[6] but is less stable than **1** and **2** for both electron counts. The s and p valence orbitals of boron do not lead to effective overlaps for a boron atom above a triangular face and therefore such capped structures are generally unfavorable for borane polyhedra.[13]

The different number of bonding molecular orbitals in **1** and **2** is not accidental but reflects an important and general topological distinction in deltahedral boranes, which can be interpreted by using Stone's tensor surface harmonic theory. For spherical deltahedral borane clusters that belong to the S_{4m} and D_{md} point groups, the tangential p^{π} orbitals give rise to a symmetric distribution of $n\bar{L}^{\pi}$ bonding and nL^{π} antibonding molecular orbitals. In contrast spherical clusters belonging to the C_{mv} point groups

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(1) Greenwood, N. N. *Pure Appl. Chem.* **1983**, *55*, 77-87, 1415-1430.

(2) Barker, G. K.; Garcia, M. P.; Green, M.; Stone, F. G. A.; Bassett, J. M.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1981**, 653-655.

(3) Bould, J.; Greenwood, N. N.; Kennedy, J. D.; McDonald, W. S. *J. Chem. Soc., Chem. Commun.* **1982**, 465-467.

(4) Bould, J.; Crook, J. E.; Greenwood, N. N.; Kennedy, J. D.; McDonald, W. S. *J. Chem. Soc., Chem. Commun.* **1982**, 346-348.

(5) Baker, R. T. *Inorg. Chem.* **1986**, *25*, 109-111.

(6) Mingos, D. M. P.; Forsyth, M. I. *J. Chem. Soc., Dalton Trans.* **1977**, 610-616.

(7) Kennedy, J. D. *Inorg. Chem.* **1986**, *25*, 111-112.

(8) Mingos, D. M. P. *Acc. Chem. Res.* **1984**, *17*, 311-319.

(9) Stone, A. J. *Mol. Phys.* **1980**, *41*, 1339-1354.

(10) Stone, A. J., *Inorg. Chem.* **1981**, *20*, 563-571.

(11) Stone, A. J. *Polyhedron* **1984**, *3*, 1299-1308.

(12) For a description of the extended Hückel molecular orbital calculations used in this paper see: Mingos, D. M. P. *J. Chem. Soc., Dalton Trans.* **1977**, 602-610. The B, C, H, and O parameters are described in this paper. For Rh the H_{ii} parameters are -12.50 (4d), -8.09 (5s), and -4.57 (5p) eV. The cluster geometries were based on B-B = 1.70 Å, Rh-C = 1.80 Å, C-O = 1.10 Å, and Rh-B = 2.17 and 2.40 Å.

(13) Jemmis, E. D. *J. Am. Chem. Soc.* **1982**, *104*, 7017-7020.

0020-1669/86/1325-3321$01.50/0