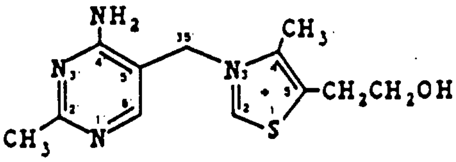
Contribution from the Department of Chemistry,
University of Hawaii at Manoa,
Honolulu, Hawaii 96822

Structure of (24-Pyrimidinium Crown-6)[(DMSO)HgI$_3$][HgI$_4$][Hg$_2$I$_7$]·11DMSO·2H$_2$O

Roger E. Cramer* and Michel J. J. Carrié

Received July 11, 1989

The rapid destruction of thiamin (vitamin B$_1$)



by sulfite ion in aqueous solution was first observed by Williams.[1] In 1974, Shimahara[2] reported oligomerization resulting from thiazole displacement by the pyrimidine ring of thiamin upon reflux in alcohols. He isolated a solid product that he inferred to be a pyrimidinium pentamer on the basis of chemical analysis and mass spectrometry. While studying the mechanism of this reaction, Zoltewicz later reported[3] that thiamin undergoes a cleavage reaction that proceeds via a second-order nucleophilic displacement, with thiazole as the leaving group. The propagation of this reaction results in the buildup of higher molecular weight oligomers in solution. Here we report the synthesis and the ^{1}H NMR and X-ray diffraction characterization of (24-pyrimidinium crown-6)[(DMSO)HgI$_3$][HgI$_4$][Hg$_2$I$_7$]·11DMSO·2H$_2$O, which is the result of such thiamin oligomerization in the presence of HgI$_2$ in acetone. This is also the first report of the [Hg$_2$I$_7$]$^{3-}$ ion.

Experimental Section

A 0.5-g (1-mmol) amount of HgI$_2$ was dissolved in 30 mL of acetone, resulting in a very faint yellow solution to which 0.432 g (1 mmol) of solid white crystalline thiamin iodide was added.[4] Stirring of the mixture at reflux in acetone for 5 min resulted in a clear yellow solution. This solution was evaporated to dryness, yielding a foamy substance that was crystallized from acetone by ether diffusion. The resulting bright yellow polycrystalline material was subsequently recrystallized from a 50/50 H$_2$O/DMSO solution. Anal. Calcd for C$_{60}$H$_{124}$N$_{18}$Hg$_4$I$_{14}$O$_{14}$S$_{12}$: C, 16.82; N, 5.88; H, 2.91. Found:[5] C, 16.70; N, 5.81; H, 2.70.

Crystals suitable for X-ray diffraction were deposited after 3 days by slow evaporation of a 20-mg solution of the compound in 1 mL of a 50/50 H$_2$O/DMSO solution. A clear yellow thick plate with maximal dimensions 0.3 × 0.25 × 0.2 mm was inserted into a capillary, and data were collected on a Nicolet R3mv diffractometer. Two data sets were collected, one at 300 K and another at 173 K. All parameters reported here were derived from the low-temperature data set. The cell parameters and their standard deviations were determined by a least-squares fit of the angular coordinates of 26 unique reflections with 2θ values ranging from 6.1 to 34.9°. Data collection parameters are shown in Table III. A decay correction was applied to all data on the basis of the variation in the intensity of three check reflections, which were measured every 100 reflections and which varied at most 9%. Data were corrected for Lorentz and polarization effects as well as for absorption, on the basis of four ψ scans with 2θ values of 9.2, 15.3, 18.6, and 21.9°. Only intensities for which $I > 3\sigma(I)$ were used in the solution and refinement of the structure.

The structure was first solved in $P\bar{1}$ by using the data set collected at 25 °C and employing heavy-atom methods. The Patterson map revealed the position of Hg(1) and its coordination sphere composed of four iodides, one located on a special position at 0, $^1/_2$, $^1/_2$. Least-squares refinement of these four atomic positions led to the location of a second mercury, which we called Hg(2), and three of its coordinated iodides. Refinement of this model lowered R from 0.56 to 0.33. In the following difference Fourier map, I(24) located on the special position $^1/_2$, 0, 0 and the atoms belonging to the three pyrimidinium rings forming the hexamer asymmetric unit were identified and their positions refined, further lowering R to 0.22. The following difference Fourier maps revealed the presence of six DMSO molecules. Refining their positions led to R = 0.19. The large thermal parameters observed for most of the solvent atoms and the presence of strong peaks in the vicinity of the sulfur positions suggested that anisotropic refinement would be appropriate. Accordingly, all Hg, I, and S positions were refined anisotropically, resulting in R = 0.11, but the DMSO thermal parameters remained large and the strong peaks near the sulfur atoms did not disappear. We also observed that I(14) and Hg(2) had unusually large thermal parameters. Since the two biggest peaks in the map, equivalent to about 5 e/Å^3, were located symmetrically on each side of the Hg(2) position, less than 1 Å away from it, we removed the Hg(2) position and replaced it with these two peaks while refining their occupancy. They successfully refined to an occupancy of 0.5 each, with thermal parameters comparable to the one calculated for Hg(1); the peak corresponding to the former Hg(2) position did not reappear. The R value decreased significantly, indicating that this model with disordered positions for Hg(2) was preferred. The large thermal parameters of the sulfur atoms prompted us to refine their occupancies. This did not, however, yield usable results, suggesting that either some degree of disorder and/or extensive thermal motion was the reason for these high thermal parameters. We subsequently decided to work with a data set collected at low temperature.

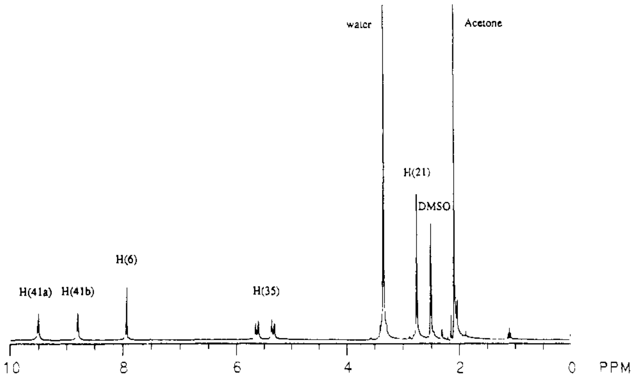


Figure 1. 300-MHz ^{1}H NMR spectrum of (24-pyrimidinium crown-6)[(DMSO)HgI$_3$][HgI$_4$][Hg$_2$I$_7$]·11DMSO·2H$_2$O in acetone-d_6.

Refinement using the low-temperature data set resulted in R = 0.0803 and much cleaner difference maps in the regions of most of the DMSO sulfur atoms. However, the disorder of the Hg(2) and two of the DMSO sulfur positions remained. In an attempt to solve these problems, we refined the structure in the lower symmetry space group, $P1$. As this did not improve the I(14) thermal parameter, the disorder in the DMSO's, or the Hg(2) disorder, and since the R value did not improve, we returned to the $P\bar{1}$ space group. While the positions for DMSO's 1, 2, 4, and 5 refine satisfactorily with a simple model where each atom is attributed one position, we had to use a somewhat more sophisticated model to account for DMSO's 3 and 6. Each of the two sulfurs was refined as two independent positions corresponding to the two strongest peaks in their vicinity, with a variable occupancy. The sulfur of DMSO 3 successfully refined as two independent positions S(3A) and S(3B), with occupancies of 0.7 and 0.3, respectively, while O(3), C(3), and C(3′) refined as fully occupied atoms. DMSO 6, which is coordinated to Hg(2B), shows yet a greater degree of disorder. We dealt with this problem by first refining the coordinating O(6) as a fully occupied atom while each of the sulfur and the carbon atoms was refined as two independent half-occupied atoms, giving rise to two independent DMSO molecules having the O(6) position in common. As some degree of disorder persisted in the carbon atom positions around S(6) and S(6′) using this model, we subsequently refined their positions while constraining the S–C and C–C distances to 1.8 and 2.8 Å, respectively. DMSO's 1, 2, 4, and 5 are not disordered so the corresponding sulfur atoms were successfully refined anisotropically. The subsequent difference Fourier map revealed the presence of a strong isolated peak, which we refined as an oxygen atom of a water molecule.

With the refinement of all hexamer atoms with a common thermal parameter, R_1 converged to 0.044 and R_2 converged to 0.053. After the last cycle of refinement, all 310 parameters shifted by less than 0.5% of their esd's, with the biggest remaining peak, equivalent to about 1.1 e, located in the vicinity of S(6).

---

(1) Williams, R. R. *J. Am. Chem. Soc.* **1935**, *57*, 229.

(2) Shimahara, N.; Asakawa, H.; Kawamatsu, Y.; Hirano, H. *Chem. Pharm. Bull.* **1974**, *22*, 2086.

(3) Zoltewicz, J. A.; Uray, G.; Kauffman, G. M. *J. Am. Chem. Soc.* **1980**, *102*, 3653.

(4) Thiamin iodide is easily prepared by adding KI to a solution of thiamin chloride. The iodide salt precipitates from solution and may be filtered and dried.

(5) Oneida Research Services Inc., One Halsey Rd, Whitesboro, NY 13492.

0020-1669/90/1329-3902$02.50/0

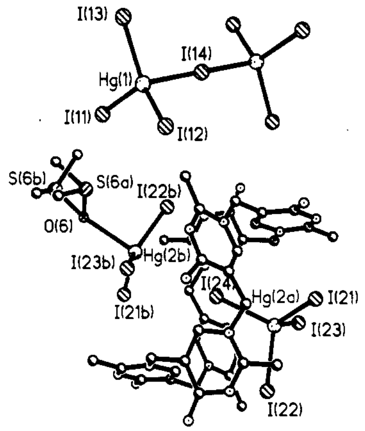


Figure 2. Perspective view of the (24-pyrimidinium crown-6)$^{6+}$ cation associated with the $[(DMSO)HgI_3]^-$ and $[HgI_4]^{2-}$ anions, as well as the lattice $[Hg_2I_7]^{3-}$ anion. A disordered DMSO coordinated to Hg(2b) is shown. Only one of the two inversion-related orientations of the $[(DMSO)HgI_3]^-$ and $[HgI_4]^{2-}$ ions is shown. Both I(24) and I(14) are located on inversion centers.

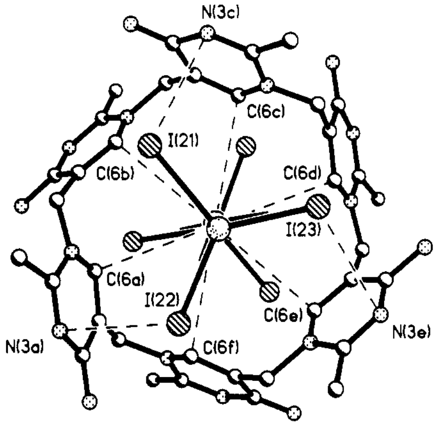


Figure 3. Perspective view down the pseudo-3-fold axis of the cyclic hexameric cation. Closest contacts between the iodo ligands and the cation are indicated by dotted lines. The atoms in the (24-pyrimidinium crown-6)$^{6+}$ hexamer are numbered according to the system shown for thiamin in the text, while the rings are denoted a–f. The unlabeled iodo ligands are related to I(21), I(22), and I(23) by inversion.

Results

The ^{1}H NMR spectrum (Figure 1) of this compound in acetone-d_6 shows only resonances due to the pyrimidinium portion of thiamin: two singlets for the exocyclic N(41) protons, one H(6) singlet, one H(21) singlet, and finally an AB quartet for the C(35) methylene bridge protons. The spectrum resembles those reported earlier for pyrimidinium oligomers from the decomposition of thiamin,[2,3] and its simplicity suggested a cyclic compound in which each monomeric unit is identical.

The X-ray data set is small with a 2θ limit of 30°. This is probably due to the large amount of solvent with high thermal parameters and some disorder. This, coupled with the presence of several heavy atoms, limits the accuracy of the parameters for the light atoms. Nevertheless, the main structural features are clear.

At 300 K most of the DMSO solvent molecules are inversion disordered with the sulfur atom occupying positions on either side of the plane defined by the two carbons and the oxygens, while at 173 K only one DMSO exhibits such disorder. Evidence of a phase change with a transition temperature near a 270 K is provided by electrical resistance measurements on a single crystal, which show an abrupt increase in resistance from 10^8 Ω at 300 K to 10^{10} Ω at 260 K, with little further change down to 77 K.

The thiamin oligomerization leads to the formation of a cyclic hexamer, which we have named (24-pyrimidinium crown-6)$^{6+}$ and which is presented in Figures 2 and 3. In this structure, charge balance results from the presence of three anions, $[(DMSO)HgI_3]^-$ and $[HgI_4]^{2-}$, which are associated with the hexamer, and an $[Hg_2I_7]^{3-}$ anion. In addition, ten DMSO molecules are hydrogen bonded to the hexamer, and two centrosymmetrically related water molecules are hydrogen bonded to DMSO molecules. Another DMSO molecule is loosely associated with the $[HgI_4]^{2-}$ anion.

Table I. Bond Distances (Å) in the Anions of (24-Pyrimidinium Crown-6)$[(DMSO)HgI_3][HgI_4][Hg_2I_7]\cdot 11DMSO\cdot 2H_2O$

Hg(1)–I(11)	2.734 (3)	Hg(2A)–I(23)	2.878 (4)
Hg(1)–I(12)	2.749 (4)	Hg(2A)–I(24)	2.845 (4)
Hg(1)–I(13)	2.745 (2)	Hg(2B)–O(6)	2.75 (5)
Hg(1)–I(14)	2.903 (2)	Hg(2B)–I(21)	2.765 (3)
Hg(2A)–I(21)	2.734 (4)	Hg(2B)–I(22)	2.611 (4)
Hg(2A)–I(22)	2.874 (4)	Hg(2B)–I(23)	2.615 (4)

Table II. Bond Angles (deg) in the Anions of (24-Pyrimidinium Crown-6)$[(DMSO)HgI_3][HgI_4][Hg_2I_7]\cdot 11DMSO\cdot 2H_2O$

I(11)–Hg(1)–I(12)	115.5 (1)	I(22)–Hg(2A)–I(24)	107.9 (1)
I(11)–Hg(1)–I(13)	115.9 (1)	I(23)–Hg(2A)–I(24)	112.3 (1)
I(12)–Hg(1)–I(13)	110.6 (1)	O(6)–Hg(2B)–I(21)	105 (1)
I(11)–Hg(1)–I(14)	102.8 (1)	O(6)–Hg(2B)–I(22)	90 (1)
I(12)–Hg(1)–I(14)	104.5 (1)	O(6)–Hg(2B)–I(23)	92 (1)
I(13)–Hg(1)–I(14)	106.1 (1)	I(21)–Hg(2B)–I(22)	115.8 (1)
I(21)–Hg(2A)–I(22)	108.6 (1)	I(21)–Hg(2B)–I(23)	116.8 (1)
I(21)–Hg(2A)–I(23)	109.5 (1)	I(22)–Hg(2B)–I(23)	124.7 (1)
I(22)–Hg(2A)–I(23)	107.1 (1)	Hg(2B)–Hg(2A)–I(24)	170.3 (1)
I(21)–Hg(2A)–I(24)	111.3 (1)		

Table III. Summary of Crystal and Data Collection Parameters for (24-Pyrimidinium Crown-6)$[(DMSO)HgI_3][HgI_4][Hg_2I_7]\cdot 11DMSO\cdot 2H_2O$

compd	(24-pyrimidinium crown-6)$[(DMSO)HgI_3][HgI_4][Hg_2I_7]\cdot 11DMSO\cdot 2H_2O$
formula	$C_{60}H_{124}N_{18}O_{14}S_{12}Hg_4I_{14}$
fw	4285.15
a, Å	13.220 (5),[a] 13.308 (4)[b]
b, Å	15.677 (3),[a] 15.693 (5)[b]
c, Å	16.248 (3),[a] 16.618 (9)[b]
α, deg	68.11 (1),[a] 68.86 (3)[b]
β, deg	80.42 (2),[a] 80.39 (4)[b]
γ, deg	89.81 (2),[a] 89.63 (3)[b]
V, Å^3	3074 (1),[a] 3186 (2)[b]
Z	1
dens, g/cm^3	2.31 (calcd)
space group	$P\bar{1}$
radiation	Mo Kα
cryst dimens, mm	0.3 × 0.25 × 0.2
μ, cm^{-1}	86.6
transm coeff	0.341–0.442
2θ limits, deg	3.0–30.0
tot. no. of observns	2398
no. of unique data used ($I > 3\sigma(I)$)	1834
final no. of variables	310
R_1[c]	0.044
R_2[d]	0.053
overdetermination ratio	5.9
goodness-of-fit	1.25

[a] −100 °C. [b] 25 °C. [c] $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$. [d] $R_2 = \sum[(||F_o| - |F_c||)w^{1/2}]/\sum(|F_o|w^{1/2})$.

Bond distances and bond angles within each pyrimidinium moiety are similar to those observed in protonated thiamin.[6] Alternating pyrimidiniums are related by a noncrystallographic 3-fold axis (Figure 3), and consecutive pyrimidinium planes are nearly perpendicular, as indicated by their dihedral angle, which averages 105°. The cavity in the center of the hexamer has a diameter of about 4.0 Å, which allows it to host bulky anions. In this structure, an iodo ligand, I(24), resides on the inversion center located at the center of the cavity. The closest contacts of this iodo ligand to the hexamer ring are with the C(6) atoms and range from 3.69 to 3.71 Å. Six other iodo ligands, arranged in cen-

---

(6) Cramer, R. E.; Maynard, R. B.; Ibers, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 76.

trosymmetric pairs and designated I(21), I(22), and I(23), are also near the hexamer with the closest approaches being to the N(3) pyrimidinium positions at 3.59–3.73 Å. Both of the disordered positions for Hg(2) are within bonding distance of I(21), I(22), and I(23), while only one of them, Hg(2a), is bound to I(24). Upon comparison of the Hg–I bond distances (Table I) and angles (Table II) with those previously reported for $[HgI_4]^{2-}$[7,8] and $[HgI_3]^{-}$,[8,9] we concluded that two anions, $[HgI_4]^{2-}$ and $[(DMSO)HgI_3]^{-}$, are associated with the hexamer, one to the right and one to the left, as shown in Figure 2. However, since I(24) occupies a center of symmetry, these two anions are disordered in the lattice with each taking the left-hand position in half of the unit cells and the right-hand position in the remaining half. The Hg(II) ion in the $[HgI_3]^{-}$ ion is further coordinated by DMSO 6 at a Hg(2b)–O(6) distance of 2.75 (5) Å, which is longer than Hg–O separations in similar compounds.[10]

A third anion, $[Hg_2I_7]^{3-}$, is located in the lattice, fairly isolated from any other component of the structure (Figure 2). This is to our knowledge the first structural report of this mercury(II) polyiodide ion. The geometry about the Hg(1) ion is nearly tetrahedral (Table I), and the bridging I(14) is located on an inversion center. The bridging role of I(14) results in a Hg(1)–I(14) distance about 0.15 Å longer than the average terminal Hg(1)–I distance. This is consistent with what is observed in $[Hg_2I_6]^{2-}$.[11] Accordingly, the terminal I–Hg(1)–I(14) [I = I(11), I(12), I(13)] angles are significantly smaller than the remaining I–Hg(1)–I angles (Table II).

In addition to the DMSO that is coordinated to Hg(2b), there are 11 other DMSO molecules in the lattice. One of these is inversion-related to the DMSO that coordinates Hg(2b) and is loosely held, which probably accounts for the disorder found for DMSO 6. Six of the DMSO molecules, numbers 2, 4, and 5, form a "belt" around the exterior of the hexamer, with each DMSO oxygen forming a hydrogen bond to N(41) of one ring, with O–N distances ranging from 2.66 to 2.80 Å while also approaching N(1) of an adjacent pyrimidinium ring with O–N distances of 2.79–3.11 Å. Four more DMSO molecules, numbers 1 and 3, are located above and below the hexamer and are hydrogen bonded to N(41) groups of only one pyrimidinium ring at 2.83 and 2.82 Å, respectively. The two water molecules hydrogen bond at 3.09 Å to DMSO 2, which is the DMSO that hydrogen bonds most weakly to the hexamer.

The general features of the ^{1}H NMR spectrum reported here are similar to those observed for (24-pyrimidinium crown-6)-$(NO_3)_6$,[12] except for the signals due to the C(35) protons, for which we report here an AB quartet rather than the singlet observed for (24-pyrimidinium crown-6)$(NO_3)_6$. The two protons of the C(35) methylene group are not equivalent in the static structure of the hexamer. However, rapid torsion about the C(5)–C(35) and C(35)–N(1) bonds creates an average mirror plane perpendicular to the pseudo-3-fold axis of the hexamer. Such rapid rotation apparently occurs in the nitrate salt of the hexamer but not in the compound reported here. We believe this indicates that the polyiodomercurate anions remain associated with the hexamer in solution, thus blocking the ring flexing motion and producing the observed AB quartet.

With its high positive charge and large central cavity, (24-pyrimidinium crown-6)$^{6+}$ is an attractive candidate for anion complexation. Other notable properties are the ease of synthesis, minimal flexibility due to the aromatic rings, and the presence of both H-bond acceptor, N(3), and donor, N(41), sites. This work demonstrates that an iodide anion can fit into the cavity and that species such as $[HgI_4]^{2-}$ and $[(DMSO)HgI_3]^{-}$ will associate with this hexameric cation. In addition, a new anion, $[Hg_2I_7]^{3-}$, is seen here in the lattice, presumably as a result of the high positive charge on (24-pyrimidinium crown-6). Work with a number of other anions is in progress.

Supplementary Material Available: Listings of positional and thermal parameters, least-squares planes, bond distances and angles, and hydrogen bonds (10 pages); a table of final observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

---

(7) McAuliffe, C. A. *The Chemistry of Mercury*; McAuliffe, C. A., Ed.; MacMillan: London, 1977.

(8) Deacon, G. B. *Rev. Pure Appl. Chem.* **1963**, *13*, 189.

(9) Fenn, R. H.; Oldham, J. W. H.; Phillips, D. C. *Nature* **1963**, *198*, 381.

(10) In $[\mu\text{-(DMSO)HgCl}_2]_2$, the Hg–O distances are 2.52 and 2.56 Å: Biscarini, P.; Fusina, L.; Nivellini, G. D.; Mangia, A.; Pelizzi, G. *J. Chem. Soc., Dalton Trans.* **1974**, 1846.

(11) In $(I)_2Hg(I)_2Hg(I)_2$, the two terminal Hg–I distances average 2.69 Å, while the bridging Hg–I bonds range from 2.880 (4) to 2.950 (4) Å: Beurskens, P. T.; Bosman, W. P. J. H.; Cras, J. A. *J. Cryst. Mol. Struct.* **1972**, *2*, 183.

(12) Kim, E., M.S. Thesis, University of Hawaii, 1987.

Contribution from the Department of Chemistry,
University of Florida, Gainesville, Florida 32611

Oxidation of Alcohols by a Six-Coordinate Ru(IV)–O Complex

Thomas R. Cundari† and Russell S. Drago*

Received October 25, 1989

Introduction

Much research has been conducted on the mechanisms by which metal–oxo reagents oxidize organic substrates.[1] Many of the proposed mechanisms involve attack of the substrate on the oxo and oxidation of the substrate (and reduction of the metal) followed by solvolysis of the oxidized product. For example, INDO/1 analyses of epoxidations[2a] and sulfoxidations,[2b] by the same six-coordinate Ru(IV)–O complex discussed herein, reveal that the favored pathways are directed at the oxo; the metal played no direct role in the oxidation and acted only as an electron sink. The complex *cis*-$[Ru(bpy)_2(py)(O)]^{2+}$ is active for methanol oxidation.[3] MeOH (and other aliphatic alcohols) oxidation differs in some respects from those of the aromatic alcohols in that its ΔH^* (14 ± 2 kcal mol^{-1}) is higher than that of benzyl alcohol (5.7 ± 0.2 kcal mol^{-1}).[3] Unlike that of benzyl alcohol, the enthalpy of activation for methanol is temperature dependent, although only a small temperature range was studied (291–313 K). For MeOH, $k_H/k_D = 9$; the k_H/k_D for benzyl alcohol is 50![3] The rates of oxidation of benzylic alcohols are about 2 orders of magnitude greater than those for aliphatic alcohols.[3] As Meyer has proposed, the extremely high kinetic isotope effect may result from quantum-mechanical tunneling, but only in significant amounts for the benzylic alcohols while the aliphatic alcohols proceed through a classical pathway. This present study extends the previous research to the oxidation of alcohols by a Ru(IV)–O complex.[4] The intent is to see if a substrate which is a good donor will prefer pathways that directly involve the metal in the oxidation. Similar proposals have been discussed with respect to the mechanism of olefin epoxidation by η^2-peroxides.[5a,b] The mechanism for this reaction has been envisaged to occur by either precoordination of the olefin to the metal followed by addition of the metal–oxygen bond across the double bond of the olefin to yield a five-membered-ring intermediate[5a] or direct attack of the olefin on a peroxide oxygen followed by electronic rearrangement to yield epoxide product.[5b] The preferred pathway as revealed by an extended Hückel analysis of epoxidation by η^2-peroxides involves precoordination of the substrate to the metal followed by attack on a peroxide oxygen; i.e. it is a combination of both proposals.[5c]

Calculations

An MO analysis of the interaction between *cis*-$[Ru(HN{=}CH{-}HC{=}NH)_2(NH_3)(O)]^{2+}$ (hereafter referred to as RuN_5O^{2+}, Figure 1) and methanol was performed by using the INDO/1 method.[6] The calculation of open- and closed-shell species employed the unrestricted

---

† Present address: Department of Chemistry, North Dakota State University, Fargo, ND 58105-5516.

0020-1669/90/1329-3904$02.50/0