

Aerobic Oxidation of Alcohols Catalyzed by Rhodium (III) Porphyrin Complexes in Water: Reactivity and Mechanistic Studies

Lianghui Liu^a, Mengmeng Yu^a, Bradford B. Wayland^b and Xuefeng Fu^{a*}

^a Beijing National Laboratory for Molecular Sciences, State Key Lab of Rare Earth Materials

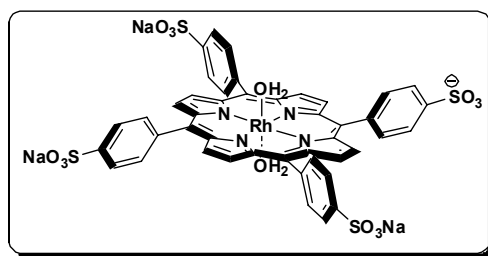
Chemistry and Applications, Peking University, Beijing, 100871, China. Fax: +86 10 6275 1708; Tel: +86 10 6275 6035; E-mail: fu xf@pku.edu.cn

^b Department of Chemistry, Temple University, Philadelphia, PA 19122, USA. Fax: +1 215 204 1532; Tel: +1 215 204 7875; E-mail: BWayland@Temple.edu

Supporting Information

General considerations: D₂O, CD₃OD, CD₃CD(OD)CD₃ was purchased from Cambridge Isotope Laboratory Inc.; tetra p-sulfonatophenyl porphyrin from Tokyo Chemical Industry (TCI); (Rh(CO)₂Cl)₂ from Stream; and all other chemicals were purchased from Aldrich or Alfa Aesar unless otherwise noted and used as received. Room temperature ¹H NMR spectra were recorded on a Bruker AV-400 spectrometer and variant temperature ¹H NMR spectra on a Bruker AV-600. The chemical shifts were referenced to 3-trimethylsilyl-1-propanesulfonic acid sodium salt.

Na₃[(TSPP)Rh^{III}(H₂O)₂]. Na₃[(TSPP)Rh^{III}(H₂O)₂] was synthesized by literature methods of Ashley¹. The stock solution of (TPPS)Rh^{III} was prepared in H₂O solution. A certain amount of stock solution was withdrawn from the stock solution into a round bottom flask and acid/base solution (CF₃SO₃H or NaOH) were added to tune the pH value. After the solvent was removed under vacuum, the mixture was dissolved in D₂O.



Scheme 1S The structure of (TSPP)Rh^{III}(H₂O)₂

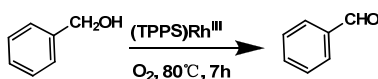
Catalytic aerobic oxidation of alcohols in water. 1.8 ml 2 mg/ml (TPPS)Rh^{III} solution was transferred into a 10 ml round bottom flask. After the solvent was removed under vacuum, the solid was dissolved in 1.5 ml buffer solution. The solution was then transferred to a Schlenk flask with a high vacuum valve (V=40 ml) fitting in a Radleys parallel synthesis station. The sample was subjected to three freeze-pump-thaw cycles after 663 μ L PhCH₂OH was added, and then filled with 1 atm O₂. The solution was stirred and heated at 80 °C for 7 h.



Figure 1S Radleys parallel synthesis station

Preparation of the buffer solutions. pH=9.2 borate buffer: 0.477 g $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ (1.25 mmol) was dissolved in water and then diluted to 25.00 ml in a 25ml volumetric flask. ($\text{H}_3\text{BO}_3/\text{NaBO}_2=0.10$ M/0.10 M). pH=10.2 carbonate buffer: 0.401 g NaHCO_3 (4.77 mmol) and 0.452 g Na_2CO_3 (4.26 mmol) was dissolved in water and then diluted to 25.00 ml in a 25ml volumetric flask. ($\text{NaHCO}_3/\text{Na}_2\text{CO}_3=0.19$ M/0.17 M). pH=11.2 carbonate buffer: 0.0525 g NaHCO_3 (0.625 mmol) and 0.59 g Na_2CO_3 (5.57 mmol) was dissolved in water and then diluted to 25.00 ml in a 25ml volumetric flask. ($\text{NaHCO}_3/\text{Na}_2\text{CO}_3=0.025$ M/0.22 M). pH=12.2 carbonate buffer: 3.74 g Na_2CO_3 (35.3 mmol) was dissolved in water and then diluted to 25.00 ml in a 25ml volumetric flask. ($\text{Na}_2\text{CO}_3=1.4$ M). pH=13.2 buffer: 0.161 g NaOH (4.03 mmol) was dissolved in water and then diluted to 25.00 ml in a 25ml volumetric flask. ($\text{NaOH}=0.16$ M). pH=14.2 buffer: 1.603 g NaOH (40.1 mmol) was dissolved in water and then diluted to 25.00 ml in a 25ml volumetric flask. ($\text{NaOH}=1.60$ M).

Table 1S Catalytic aerobic oxidation of benzyl alcohol mediated by (TPPS)Rh^{III} in water.



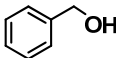
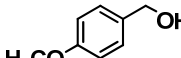
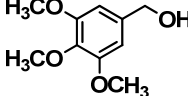
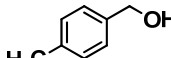
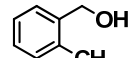
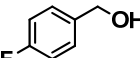
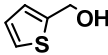
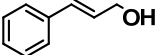
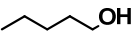



| Entry | pH | Buffer | TON | TON ^a |
|-------|------|--|-----|------------------|
| 1 | 9.2 | 0.050 M $\text{Na}_2\text{B}_4\text{O}_7$ | 60 | |
| 2 | 10.2 | 0.19 M NaHCO_3 / 0.17 M NaHCO_3 | 100 | 1360 |
| 3 | 11.2 | 0.025 M NaHCO_3 / 0.22 M NaHCO_3 | 220 | 1510 |
| 4 | 12.2 | 1.4 M Na_2CO_3 | 150 | 1460 |
| 5 | 13.2 | 0.16 M NaOH | 560 | |
| 6 | 14.2 | 1.6 M NaOH | 460 | |

Reaction condition: alcohols 0.66 ml (6.3 mmol) and 1.5 ml buffer solution containing (TPPS)Rh^{III}

3.6 mg (3.2×10^{-3} mmol) in a 40 ml tube charged with 1 atm oxygen. a: refluxing for 3 h in a 100 ml tube charged with 1 atm oxygen. TON=n(benzaldehyde)/n((TPPS)Rh^{III}), GC yield.

Measurement of solubility of each alcohol in water. The saturated solubility of each alcohol in D₂O was determined by ¹H NMR relative to a standard 3-trimethylsilyl-1 propanesulfonic acid sodium salt at room temperature.

Table 2S The physical properties of substrate alcohols

| Entry | 1 | 2 | 3 | 4 | 5 | 6 |
|---------------------------|---|---|---|--|---|---|
| Substrate |  |  |  |  |  |  |
| mp | -15 | 22 | | 59 | 34 | 22 |
| bp | 205 | 134/12mm | 228/25mm | 116/20mm | 109/14mm | 204 |
| Solubility ⁱ | 0.36 | 0.18 | 0.25 | 0.058 | 0.056 | 0.23 |
| Product bp | 178 | 247 | 163/10mm | 83/11mm | 200 | 180 |
| TON ⁱⁱ | 560 | 690 | 590 | 290 | 320 | 350 |
| Selectivity ⁱⁱ | >99% | 94% | 95% | >99% | 91% | 90% |
| Entry | 7 | 8 | 9 ⁱⁱⁱ | 10 | 11 | 12 |
| Substrate |  |  |  |  |  |  |
| mp | | 32 | -79 | -50 | -19 | 23 |
| bp | 206 | 249 | 128 | 118 | 139 | 160 |
| Solubility ⁱ | 0.44 | 0.032 | 0.27 | 0.49 | 1.1 | 0.41 |
| Product bp | 196 | 250 | 108 | 103 | 130 | 154 |
| TON ⁱⁱ | 640 | 70 | 20 | 90 | 210 | 80 |
| Selectivity ⁱⁱ | 94% | >99% | 77% | >99% | >99% | >99% |

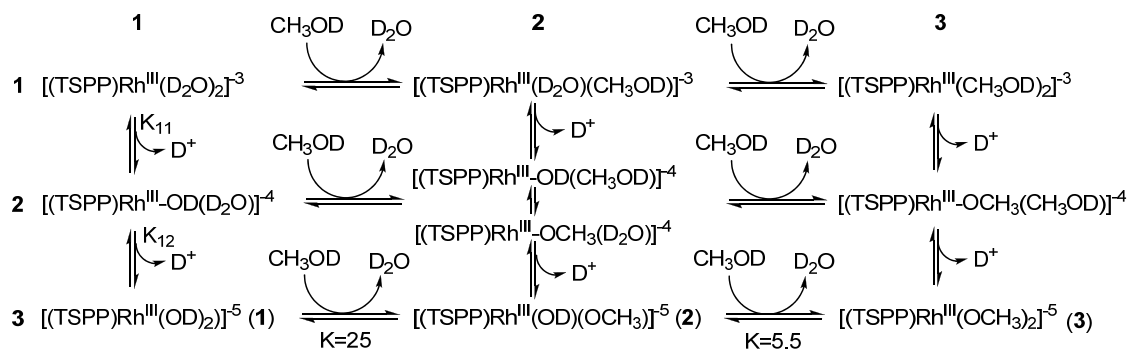
The oxidation of isopropanol without the presence of CH₃I at 40 °C (pH=11.2). 0.50 ml 2 mg/ml (TPPS)Rh^{III} solution and 0.40 ml pH=11.2 carbonate buffer solution were mixed in a 10 ml round bottom flask. After the solvent was removed under vacuum, the mixture was redissolved in 0.40 ml D₂O solution containing (CH₃)₃SiCH₂CH₂CH₂SO₃Na (3.0×10^{-3} M) in a J.Young Valve NMR tube. The sample was subjected to three freeze-pump-thaw cycles after 5 μL isopropanol was added. The kinetic ¹H NMR spectra were recorded on the Bruker AV-600 magnet at 313.2 K.

The oxidation of isopropanol in the presence of CH₃I at 40 °C (pH=11.2). 0.5 ml 2 mg/ml (TPPS)Rh^{III} solution and 0.40 ml pH=11.2 carbonate buffer solution were mixed in a 10 ml round bottom flask. After the solvent was removed under vacuum, the mixture was redissolved in 0.40 ml D₂O solution containing (CH₃)₃SiCH₂CH₂CH₂SO₃Na (3.0×10⁻³ M). The red solution was transferred to a J. Young Valve NMR tube containing an external standard benzyl aldehyde. The sample was subjected to three freeze-pump-thaw cycles after 5 μL isopropanol was added. CH₃I was transferred to the NMR tube through an 'H' tube. The kinetic ¹H NMR spectra at different concentration of isopropanol were recorded at 313.2 K, KIE comparison of regular and deuterated isopropanol was performed at 308.2 K. Activation parameters were obtained by measuring rate constants at different temperature at 303.2 K, 308.2 K, 313.2 K, and 323.2 K, respectively.

Table 3S The measurement of rate constants at different concentration of isopropanol (pH=11.2).

| Entry | Amount of isopropanol | c(isopropanol)/M | k _{obs} |
|-------|-----------------------|------------------|------------------|
| 1 | 6 μL isopropanol | 0.20 | 3.29E-4 |
| 2 | 8 μL isopropanol | 0.26 | 4.01E-4 |
| 3 | 10 μL isopropanol | 0.32 | 4.96E-4 |
| 4 | 12 μL isopropanol | 0.40 | 5.57E-4 |
| 5 | 14 μL isopropanol | 0.43 | 6.13E-4 |

The observation of porphyrin rhodium alkoxide in water. 30 μL (or 60 μL) methanol (1.4 M or 2.8 M) was added to an NMR tube containing 0.5 ml D₂O solution of (TSPP)Rh^{III} (9×10⁻⁴ M), (CH₃)₃SiCH₂CH₂CH₂SO₃Na (3.0×10⁻³ M). The ¹H NMR was recorded on a Bruker AV-400 spectrometer at room temperature. Aqueous solutions of (TSPP)Rh^{III} complexes occurs in an equilibrium distribution with the bis aquo, mono and bishydroxo complexes, [(TSPP)Rh^{III}(D₂O)₂]⁻³, [(TSPP)Rh^{III}-OD(D₂O)]⁻⁴, [(TSPP)Rh^{III}(OD)₂]⁻⁵ in water (Scheme 2S Column 1). The porphyrin pyrrole and phenyl ¹H NMR shifts are used in identifying the (TSPP)Rh species in D₂O. ¹H NMR shift and intensity measurements were used effectively in quantifying the distribution of species in solution. Mixing methanol with (TSPP)Rh^{III} in water resulted in the formation of another 9 rhodium porphyrins species, [(TSPP)Rh^{III}(D₂O)₂]⁻³, [(TSPP)Rh^{III}(D₂O)(DOCH₃)]⁻³, [(TSPP)Rh^{III}(DOCH₃)₂]⁻³, [(TSPP)Rh^{III}-OD(D₂O)]⁻⁴, [(TSPP)Rh^{III}-OD(DOCH₃)]⁻⁴/[(TSPP)Rh^{III}-OCH₃(D₂O)]⁻⁴, [(TSPP)Rh^{III}-OCH₃(D₂O)]⁻⁴, [(TSPP)Rh^{III}(OD)₂]⁻⁵, [(TSPP)Rh^{III}-OD(OCH₃)]⁻⁵, and [(TSPP)Rh^{III}(OCH₃)₂]⁻⁵. There were 12 fast equilibrium reactions involved (Scheme 2S, Figure 2S).



Scheme 2S The possible simultaneous multi-equilibrium of 9 rhodium porphyrins species with the addition of methanol in water.

Addition of methanol to the acidic aqueous solution (pH<5) containing (TSPP)Rh^{III} where [(TSPP)Rh^{III}(D₂O)₂]³⁻ predominated resulted in an equilibrium distribution with the mono and bis methanol complexes, [(TSPP)Rh^{III}(D₂O)(DOCH₃)]³⁻, [(TSPP)Rh^{III}(DOCH₃)₂]³⁻ (Scheme 2 Row 1). Investigations by ¹H NMR spectroscopy in D₂O as a function of concentration of methanol at different pH value reveal that the 3 complexes (Scheme 2 Row 1) were in fast equilibrium. Rapid interchange of coordinated water and methanol with the bulk solvent and free methanol in the solution resulted in a single set porphyrin ¹H NMR resonances (Figure 2S A). In the range of 0.001M<[NaOH]<0.02 M, 3 complexes in Scheme 2S Row 2 are dominant species and in rapid equilibrium where the ¹H NMR resonances of coordinated methoxide hydrogens shifted from -3.01 ppm to -2.88 ppm with increasing the hydroxide concentration (Scheme 2S Row 2, and Figure 2S B-D). In the range of 0.025M<[NaOH]<0.10 M, [(TSPP)Rh^{III}(OD)₂]⁵⁻(1), [(TSPP)Rh^{III}-OD(OCH₃)]⁵⁻(2), and [(TSPP)Rh^{III}(OCH₃)₂]⁵⁻(3) are in fast equilibrium distribution and the ¹H NMR resonances of coordinated mono methoxide hydrogens of **2** was found at -2.82 ppm and the bis methoxide of **3** at -2.84 ppm (Figure 2S E and Figure 3S). When the [NaOD]>0.2M, only one tiny coordinated methoxide was observed at -2.81 ppm by ¹H NMR (Figure 2S F).

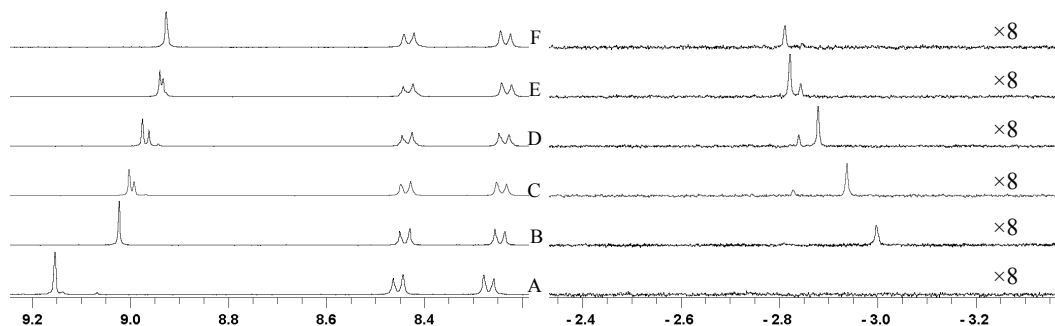


Figure 2S The ¹H NMR spectra of equilibrium distribution of 9 complexes in water at different concentration of sodium hydroxide ([(TSPP)Rh^{III}]_{initial} = 9×10⁻⁴ M, [CH₃OH] = 1.4 M). A: pH=5; B: 0.004 M NaOH; C: 0.008 M NaOH; D: 0.020 M NaOH; E: 0.025 M NaOH; F: 0.60 M NaOH.

Assignments of the ^1H NMR for 1, 2 and 3. The ^1H NMR for **1**, **2** and **3** are assigned based on the changes in the observed intensities for the pyrrole and methoxide resonance as the methanol concentration is varied (Figure 3S). The intensity integration of pyrrole hydrogens of $[(\text{TSPP})\text{Rh}^{\text{III}}\text{-OD}(\text{OCH}_3)]^{-5}$ and $[(\text{TSPP})\text{Rh}^{\text{III}}(\text{OCH}_3)_2]^{-5}$ corresponds with the intensity integration of alkoxide hydrogens (Figure 3S). With addition of methanol, the appearance of new pyrrole hydrogens at 8.93 ppm was observed with the appearance of a new resonance at -2.82 ppm which is attributed to methoxide hydrogens of complex **2** (Figure 3S C). With increasing the concentration of methanol, a new resonance of pyrrole hydrogens was observed at 8.92 ppm with the observation of high field peak at -2.84 ppm ascribed to the methoxide hydrogens of complex **3** (Figure 3S D-E).

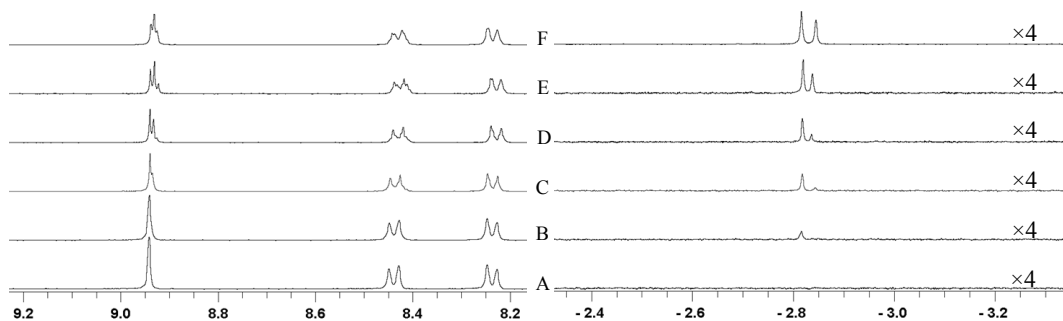
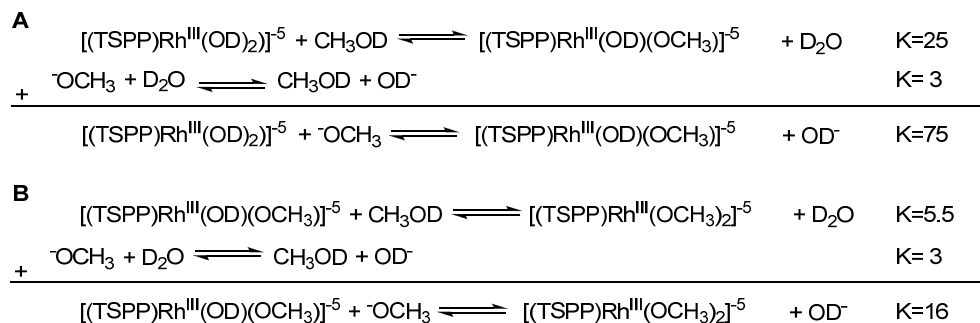


Figure 3S The ^1H NMR spectra of equilibrium distribution of complexes **1-3** in water at different concentration of methanol ($[(\text{TSPP})\text{Rh}^{\text{III}}]_{\text{initial}} = 9 \times 10^{-4} \text{ M}$, $[\text{NaOH}] = 0.030 \text{ M}$). A: without methanol; B: 0.50M methanol; C: 1.0M methanol; D: 1.4 M methanol; E: 2.9 M methanol; F: 3.8 M methanol.

The evaluation of equilibrium constant of ligand substitution reaction in water. The porphyrin pyrrole and phenyl ^1H NMR shifts are used in identifying the $(\text{TSPP})\text{Rh}$ species in D_2O . ^1H NMR shift and intensity measurements were used effectively in quantifying the distribution of species in solution. All of the 9 complexes are in fast simultaneous equilibrium in water. At basic limit ($[\text{NaOD}] > 0.025 \text{ M}$) where complexes **1**, **2**, **3** predominate, we were able to evaluate equilibrium constants for methanol substitution of the first and second water reactions $K = 25 \pm 5$ and $K = 5.5 \pm 1$, respectively (Scheme 2S Row 3, Table 4S- Table 5S) by integration of pyrrole hydrogens and methoxide hydrogens of ^1H NMR spectra of complexes **1**, **2**, **3**.

Combining with the equilibrium of methanol and hydroxide in equilibrium with methoxide and water ($\text{CH}_3\text{OH} + \text{OH}^- \rightarrow \text{CH}_3\text{O}^- + \text{H}_2\text{O}$, $K = 0.3$)^[2], the equilibrium constant for ligand displacement of the first hydroxide to methoxide is 75 (Scheme 3S A), and the displacement of the second hydroxide is 16 (Scheme 3S B)



Scheme 3S Derivation of equilibrium constants for ligand exchange reaction in water

Table 4S The measurement of equilibrium constant of $(\text{TSPP})\text{Rh}-(\text{OD})_2 + \text{CH}_3\text{OD} \rightleftharpoons (\text{TSPP})\text{Rh}-(\text{OD})(\text{OCH}_3) + \text{D}_2\text{O}$ K in water at 298K

| Entry | [NaOD]/M | [CH ₃ OD] /M | Ratio of intensity integration ⁱ | [D ₂ O] /M | K |
|-------|----------|-------------------------|---|-----------------------|----|
| 1 | 0.025 | 1.4 | 0.65 | 55.3 | 26 |
| 2 | 0.030 | 1.4 | 0.67 | 55.3 | 26 |
| 3 | 0.030 | 2.9 | 1.54 | 55.3 | 27 |
| 4 | 0.040 | 1.3 | 0.70 | 55.3 | 30 |
| 5 | 0.040 | 2.8 | 1.28 | 55.3 | 25 |
| 6 | 0.050 | 1.4 | 0.66 | 55.3 | 26 |
| 7 | 0.050 | 2.8 | 1.04 | 55.3 | 21 |

i: Ratio of intensity integration is derived from the integration of pyrrole hydrogens of $(\text{TSPP})\text{Rh}-(\text{OD})(\text{OCH}_3)$ and $(\text{TSPP})\text{Rh}-(\text{OD})_2$ species of ¹H NMR spectra.

Table 5S The measurement of equilibrium constant of $(\text{TSPP})\text{Rh}-(\text{OD})(\text{OCH}_3) + \text{CH}_3\text{OD} \rightleftharpoons (\text{TSPP})\text{Rh}-(\text{OCH}_3)_2 + \text{D}_2\text{O}$ K

| Entry | [NaOD]/M | [CH ₃ OD]/M | Ratio of intensity integration ⁱ | [D ₂ O]/M | K |
|-------|----------|------------------------|---|----------------------|-----|
| 1 | 0.025 | 1.4 | 0.16 | 55.3 | 6.3 |
| 2 | 0.030 | 1.4 | 0.16 | 55.3 | 6.3 |
| 3 | 0.030 | 2.9 | 0.27 | 55.3 | 5.1 |
| 4 | 0.040 | 1.3 | 0.15 | 55.3 | 6.4 |
| 5 | 0.040 | 2.8 | 0.30 | 55.3 | 5.9 |
| 6 | 0.050 | 1.4 | 0.15 | 55.3 | 5.9 |
| 7 | 0.050 | 2.8 | 0.26 | 55.3 | 5.1 |
| 8 | 0.10 | 1.3 | 0.13 | 55.3 | 5.5 |

i: Ratio of intensity integration is derived from the integration of methoxide hydrogens of $(\text{TSPP})\text{Rh}-(\text{OD})(\text{OCH}_3)$ and $(\text{TSPP})\text{Rh}-(\text{OCH}_3)_2$ species of ¹H NMR spectra.

Reference:

[1] Ashley K. R.; Shyu, S. B.; Leipoldt, J. G. *Inorg. Chem.* **1980**, *19*, 1613.

[2] (a) Pliego, J. R.; Riveros, J. M. *Chem. Phys. Lett.* 2000, 332, 597; (b) Zhong, Y.; Warren, G. L.; Patel, S. *Journal of Computational Chemistry* 2008, 29, 1142.