# Characteristic Vibrational Frequencies of Osmium(II) Nitrosyl Complexes Probed by Raman Spectroscopy and DFT calculations.

## Electronic Supplementary Information

Nicolas Bélanger-Desmarais,[a] Anatolie Gavriluta,[b] Jean Bernard Tommasino,[b] Christian Reber[*a] and Dominique Luneau[*b]

[*] Corresponding authors

[a] Département de Chimie, Université de Montréal, Montréal, H3C 3J7, Québec, Canada

E-mail: christian.reber@umontreal.ca

Tel: +1 514-340-4711

[b] Université Claude Bernard Lyon 1, Laboratoire des Multimatériaux et Interfaces (UMR 5615), Campus de La Doua, 69622 Villeurbanne Cedex, France

E-mail: dominique.luneau@univ-lyon1.fr

Fax: +33 472 440 618

Tel: +33 472 431 418

# Table of Contents

**Table S1.** Calculated optimized structure of singlet ground state of *cis*-[Os(NO)Cl$_4$(Hpz)]$^-$.

| Atoms | X | Y | Z |
|---|---|---|---|
| Os | -0.42923200 | 0.01506100 | 0.05987000 |
| Cl | -0.15702200 | -2.46797100 | 0.12615500 |
| Cl | -0.08880500 | -0.10314300 | -2.31645800 |
| Cl | -0.56539300 | 2.44662900 | -0.12058500 |
| Cl | -2.80471200 | -0.19662500 | -0.27854200 |
| O | -0.69512900 | 0.10496300 | 2.96423800 |
| N | 1.71027600 | 0.17027800 | 0.12584200 |
| N | 2.46912200 | -0.93829100 | 0.05392300 |
| H | 1.95321000 | -1.82506200 | 0.00069300 |
| N | -0.60154300 | 0.07401100 | 1.79635100 |
| C | 3.77902900 | -0.63064100 | 0.02879700 |
| H | 4.53231400 | -1.40272400 | -0.03278200 |
| C | 3.87515000 | 0.75323400 | 0.09689500 |
| H | 4.77672200 | 1.34770400 | 0.09923600 |
| C | 2.54761700 | 1.21136200 | 0.15213100 |
| H | 2.13546300 | 2.20886400 | 0.18937900 |

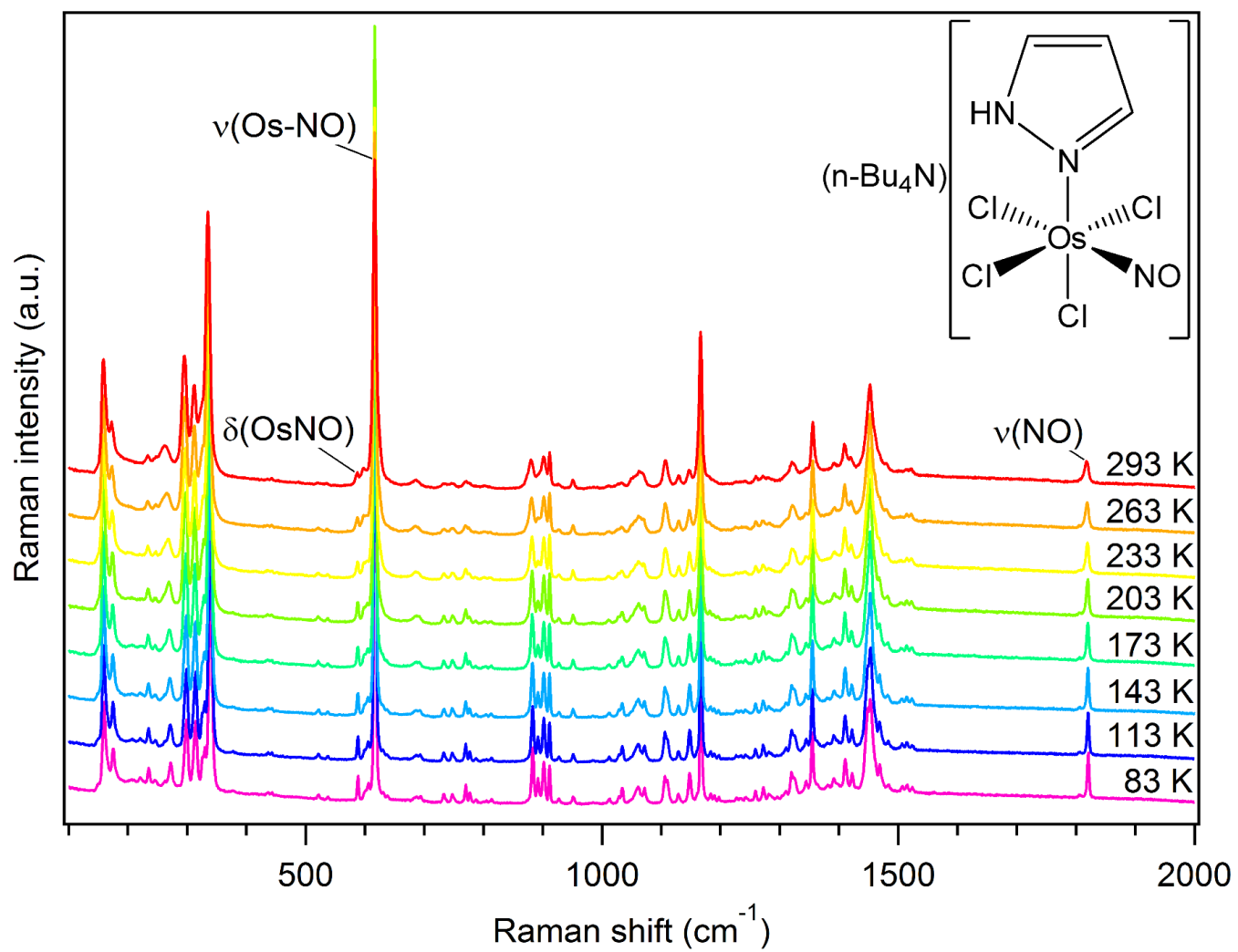**Table S2.** Calculated optimized structure of singlet ground state of *trans*-[Os(NO)Cl$_4$(Hpz)]$^-$.

| Atoms | X | Y | Z |
|---|---|---|---|
| Os | -0.50587800 | 0.00626200 | 0.00000400 |
| Cl | -0.28297400 | 0.01029800 | 2.42559500 |
| Cl | -0.17444800 | -2.44903600 | -0.00000500 |
| Cl | -0.28503900 | 0.00972800 | -2.42582500 |
| Cl | -0.52941900 | 2.43412200 | -0.00011800 |
| O | -3.39905200 | -0.23308800 | 0.00160700 |
| N | 1.68224900 | 0.15122000 | -0.00066700 |
| N | 2.44225300 | -0.95680700 | -0.00003300 |
| H | 1.93472300 | -1.84681400 | 0.00042700 |
| N | -2.23584400 | -0.13188300 | 0.00082400 |
| C | 3.75251800 | -0.65282400 | 0.00014900 |
| H | 4.50402300 | -1.42900600 | 0.00069000 |
| C | 3.84901400 | 0.73235300 | -0.00044200 |
| H | 4.75018300 | 1.32727000 | -0.00056700 |
| C | 2.52144200 | 1.19092600 | -0.00089400 |
| H | 2.11372800 | 2.19000200 | -0.00143600 |

**Table S3.** Comparison of selected bond lengths and angles of *cis*-(*n*-Bu$_4$N)[Os(NO)Cl$_4$(Hpz)] obtained from the published crystal structure with the calculated values obtained by DFT calculation on the isolated anionic complex in the gas phase at the B3LYP/MWB60(Os)/6-31G*(other atoms) level of theory (Gaussian 09).
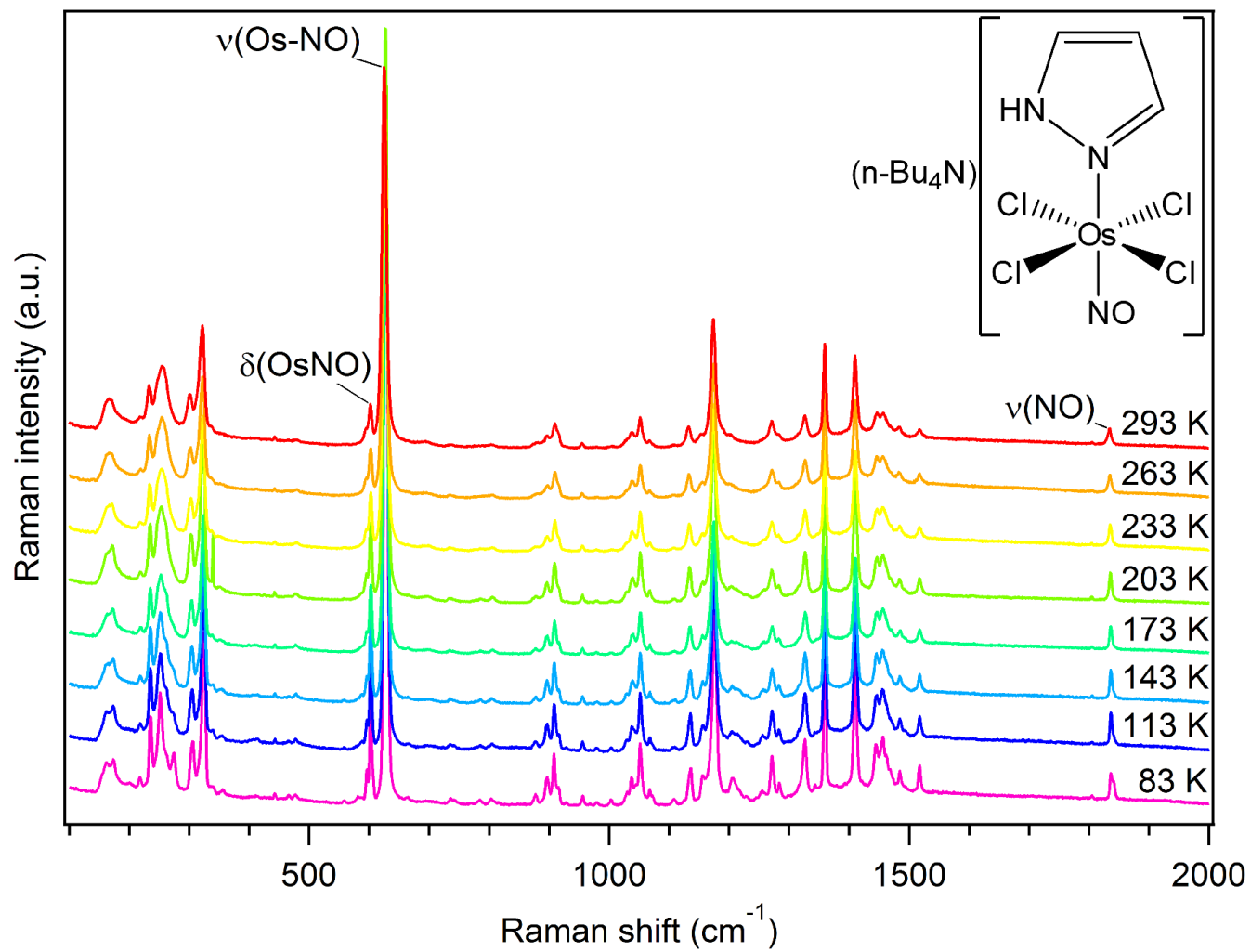
| Geometric parameters | Exp. | Calc. | Diff. (%) |
|---|---|---|---|
| Os-N(Hpz) bond length (Å) | 2.082(3) | 2.146 | 3.1 |
| Average of Os-Cl$_{eq}$ bond lengths (Å) | 2.367(1) | 2.450 | 3.5 |
| Os-Cl$_{ax}$ bond length (Å) | 2.3695(11) | 2.404 | 1.4 |
| Os-N(NO) bond length (Å) | 1.733(4) | 1.746 | 0.8 |
| N-O bond length (Å) | 1.153(4) | 1.172 | 1.7 |
| Os−N−O angle (°) | 178.1(3) | 178.8 | 0.4 |

**Table S4.** Comparison of selected bond lengths and angles of *trans*-(*n*-Bu$_4$N)[Os(NO)Cl$_4$(Hpz)] obtained from the published crystal structure with the calculated values obtained by DFT calculation on the isolated anionic complex in the gas phase at the B3LYP/MWB60(Os)/6-31G*(other atoms) level of theory (Gaussian 09).
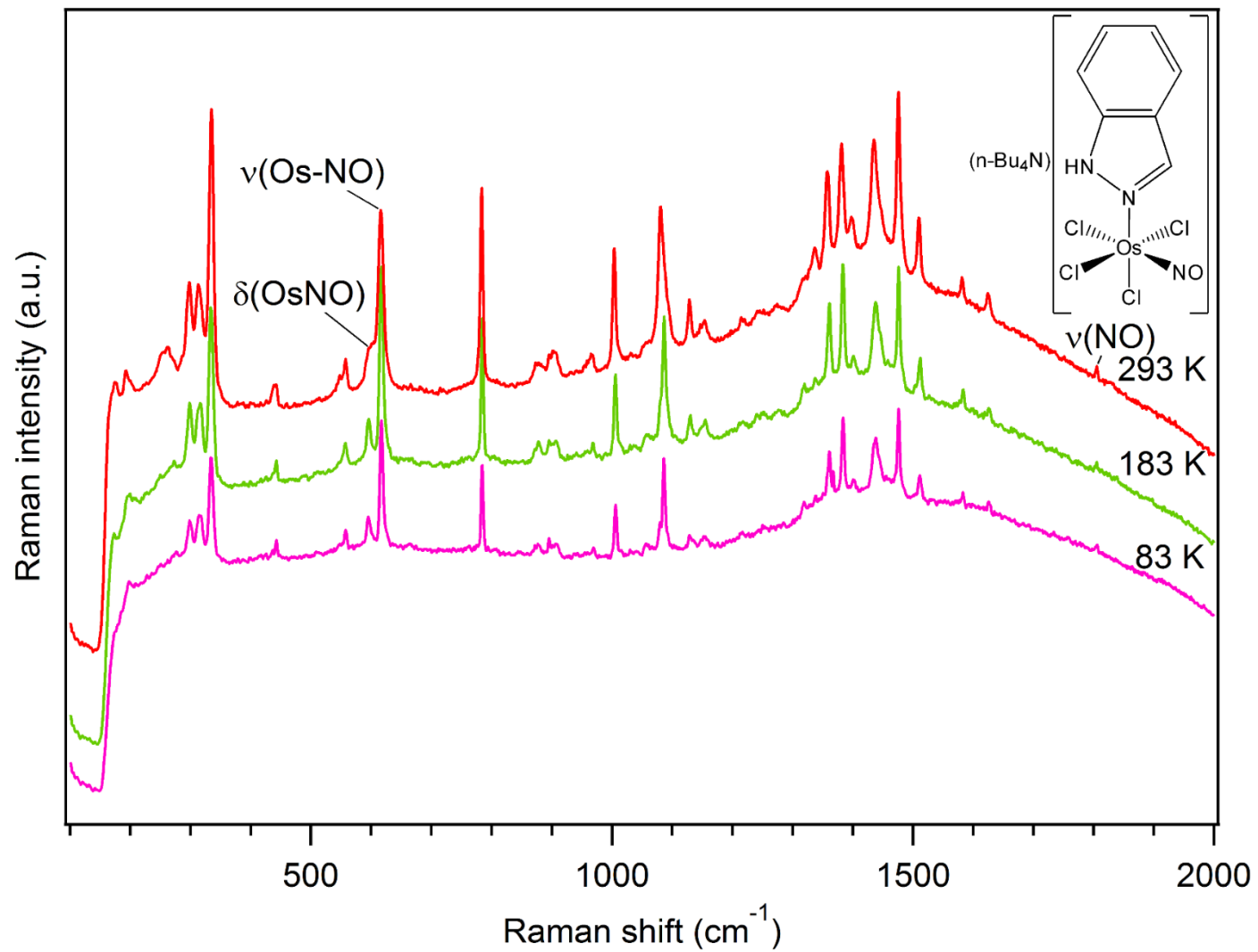
| Geometric parameters | Exp. | Calc. | Diff. (%) |
|---|---|---|---|
| Os-N(Hpz) bond length (Å) | 2.116(3) | 2.193 | 3.6 |
| Average of Os-Cl$_{eq}$ bond lengths (Å) | 2.368(1) | 2.444 | 3.2 |
| Os-N(NO) bond length (Å) | 1.736(4) | 1.735 | -0.1 |
| N-O bond length (Å) | 1.136(4) | 1.168 | 2.8 |
| Os−N−O angle (°) | 176.6(4) | 179.6 | 1.7 |

**Figure S1.** Temperature-dependent Raman spectra (λ_exc = 785 nm) of *cis*-(*n*-Bu₄N)[Os(NO)Cl₄(Hpz)] (**1**).
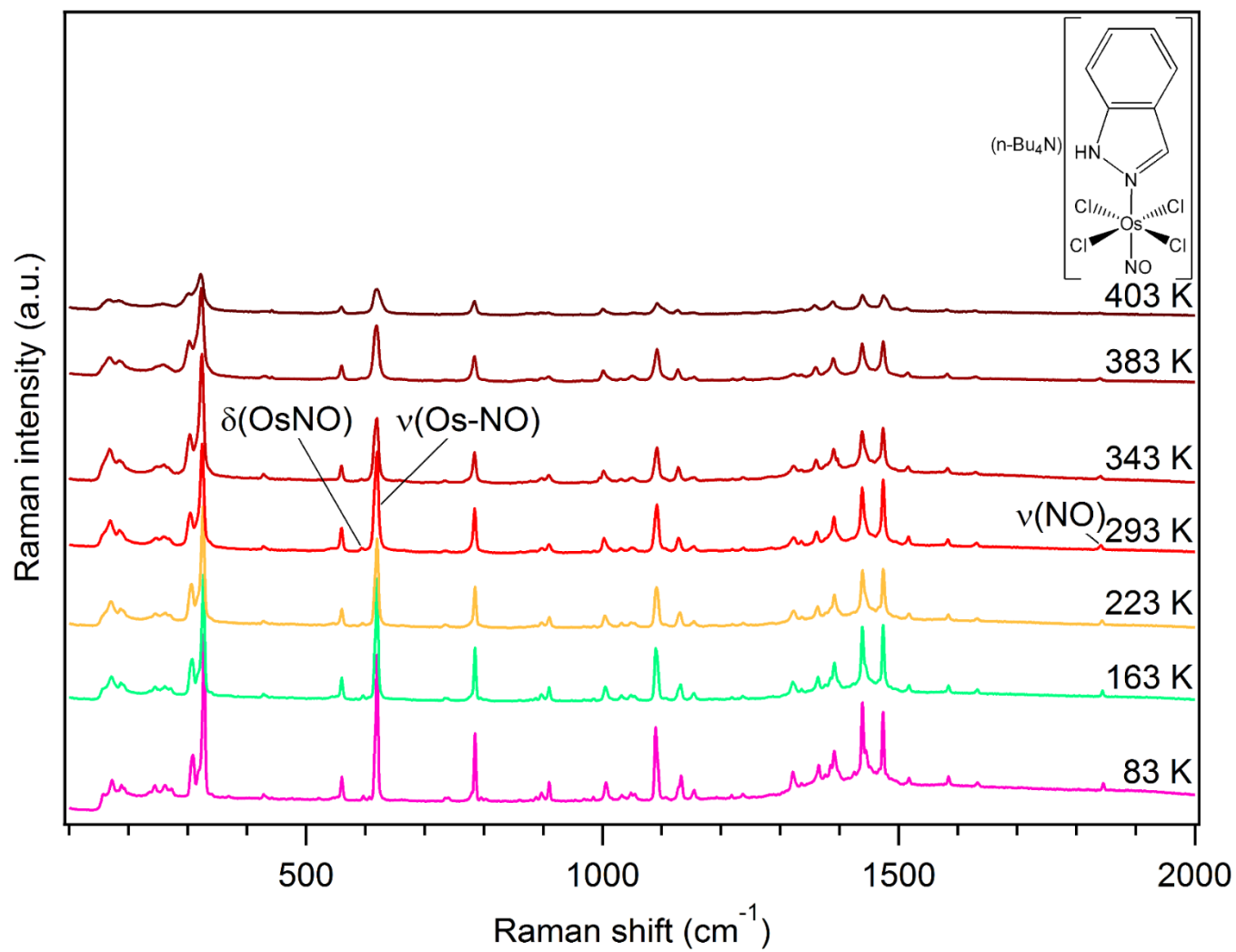
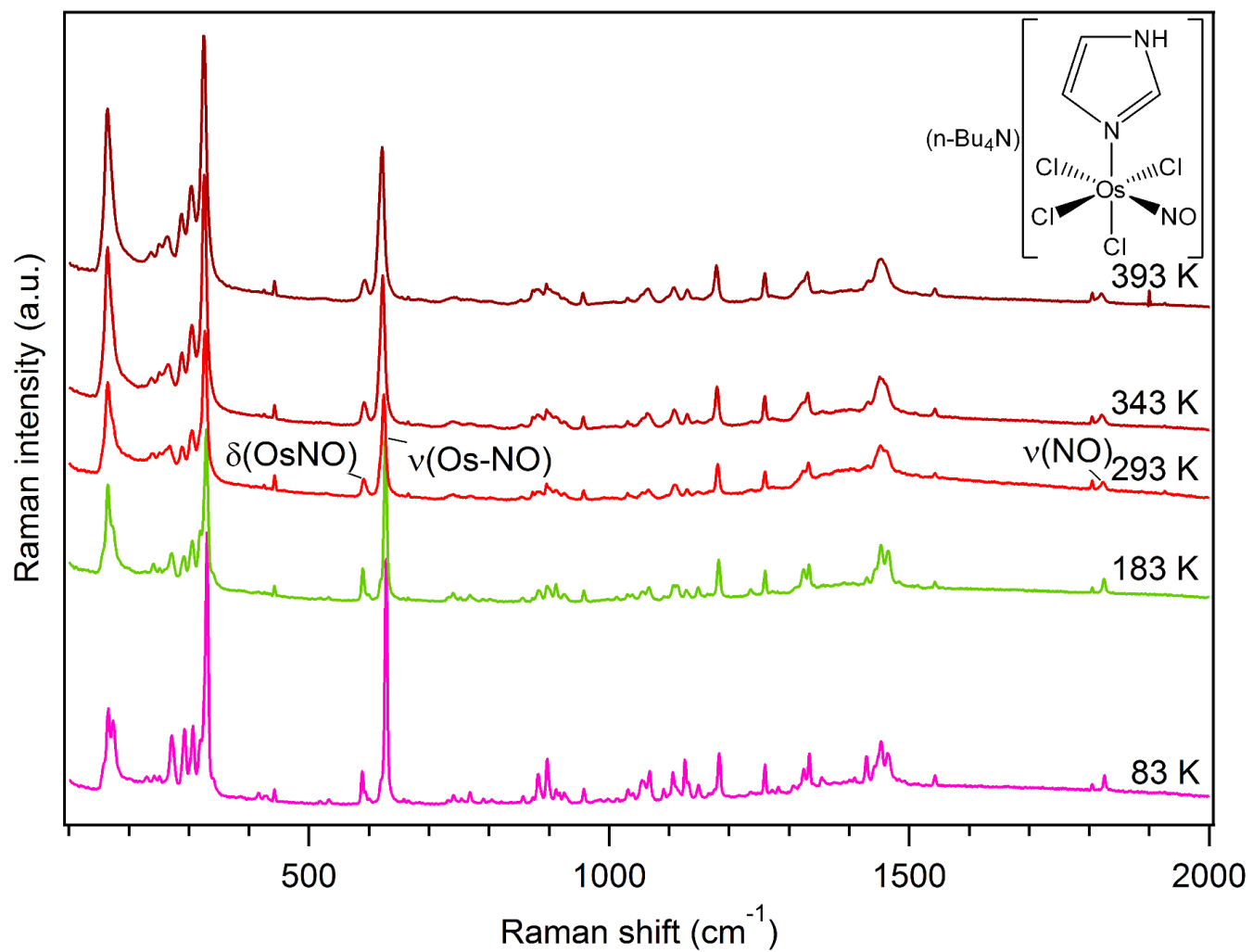**Figure S2.** Temperature-dependent Raman spectra ($\lambda_{exc}$ = 785 nm) of *trans*-(*n*-Bu$_4$N)[Os(NO)Cl$_4$(Hpz)] (**2**).

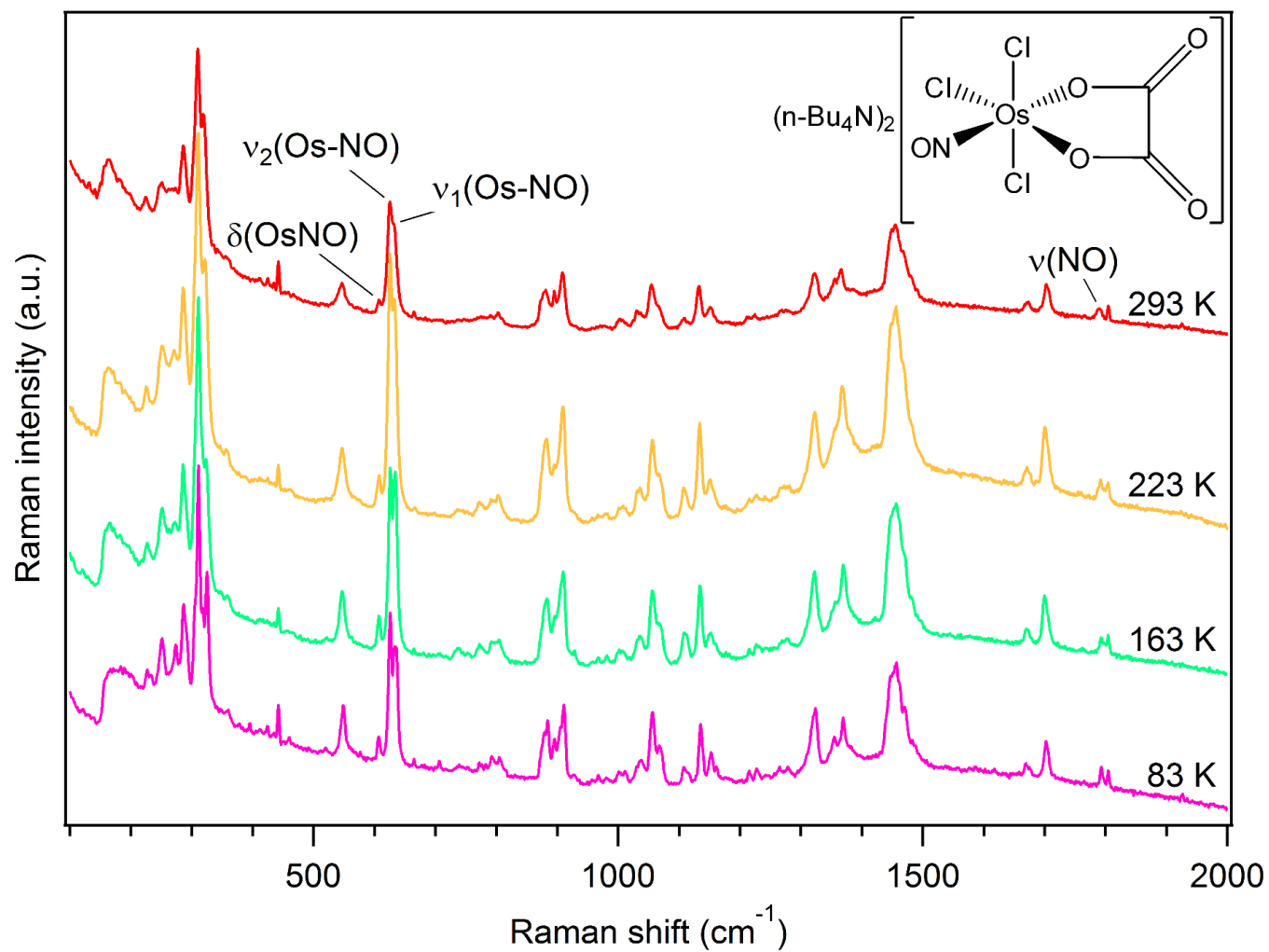**Figure S3.** Temperature-dependent Raman spectra ($\lambda_{exc}$ = 785 nm) of *cis*-(n-Bu$_4$N)[Os(NO)Cl$_4$(Hind)] (**3**).

**Figure S4.** Temperature-dependent Raman spectra ($\lambda_{exc}$ = 785 nm) of *trans*-(n-Bu$_4$N)[Os(NO)Cl$_4$(Hind)] (**4**).

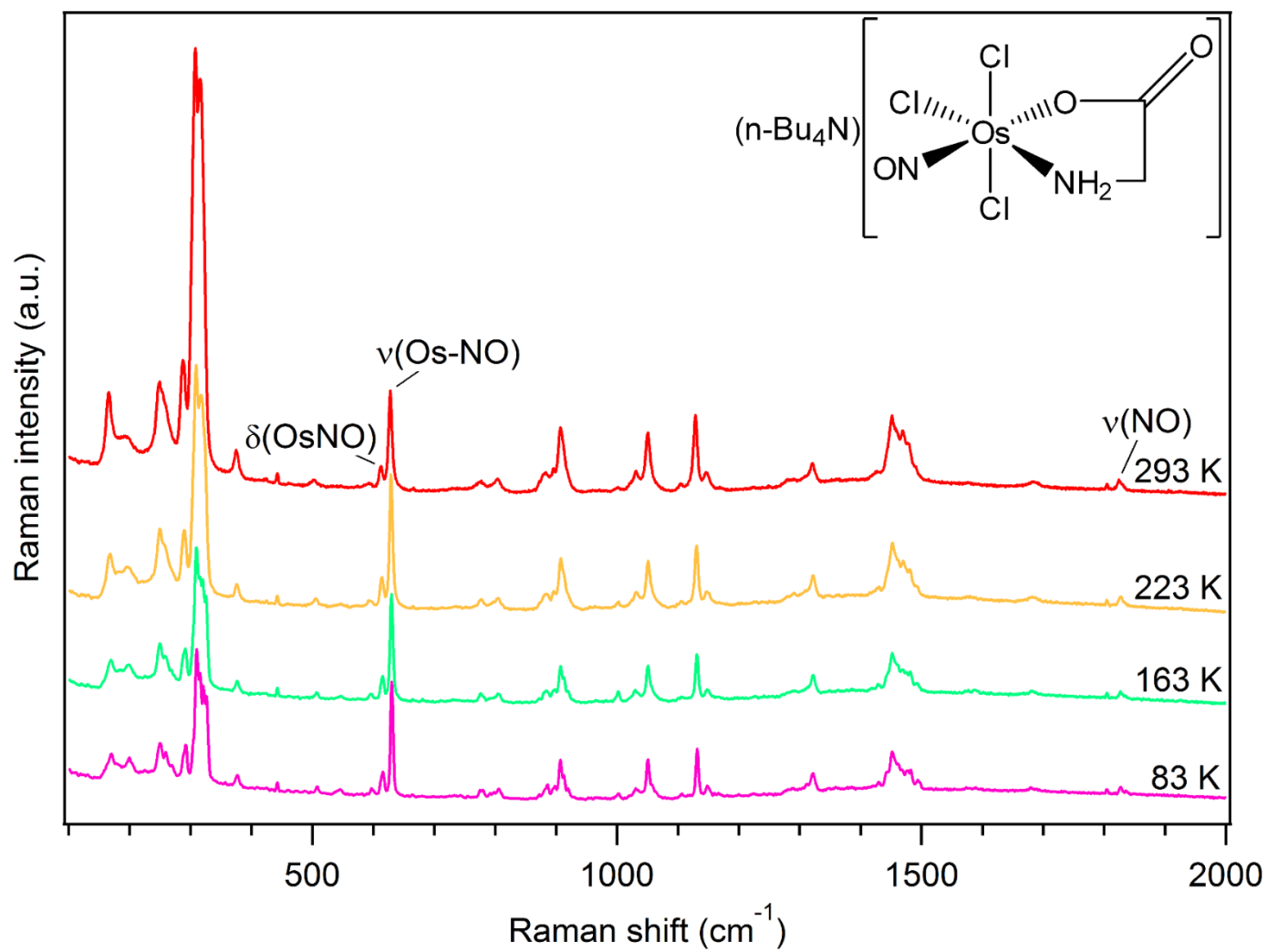**Figure S5.** Temperature-dependent Raman spectra ($\lambda_{exc}$ = 785 nm) of *cis*-(n-Bu$_4$N)[Os(NO)Cl$_4$(Him)] (**5**).

**Figure S6.** Temperature-dependent Raman spectra ($\lambda_{exc}$ = 785 nm) of *mer*(Cl), *trans*-(NO,O)-(n-Bu$_4$N)$_2$[Os(NO)Cl$_3$(ox)] (**6**).

**Figure S7.** Temperature-dependent Raman spectra ($\lambda_{exc}$ = 785 nm) of *mer*(Cl), *trans*-(NO,O)-(n-Bu₄N)[Os(NO)Cl₃(gly)] (**7**).