Electronic Supplementary Information for . . .   .

Structural Determination of Arginine-Linked Cisplatin Complexes via IRMPD Action Spectroscopy: Arginine Binds to Platinum via NO⁻-Binding Mode

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Figure Captions

Figure S1. IRMPD spectra of the $[(Arg–H)PtCl_2]^-$ and $[(Arg)PtCl_2+Na]^+$ complexes in the fingerprint region measured under variable attenuation of the FEL.

Figure S2. Binding modes of Arg to the Pt center of the $[(Arg–H)PtCl_2]^-$ complex and the designated nomenclature.

Figure S3. Binding modes of Arg to the Pt center with possible sodium binding modes of the $[(Arg)PtCl_2+Na]^+$ complex and the designated nomenclature.

Figure S4. Stable low-energy conformers of the $[(Arg–H)PtCl_2]^-$ complex and their relative Gibbs energies at 298 K calculated at B3LYP/mDZP/def2-TZVP level of theory. Structures are classified by the Arg binding mode to Pt.

Figure S5. Stable low-energy conformers of the $[(Arg)PtCl_2+Na]^+$ complex and their relative Gibbs energies at 298 K calculated at B3LYP/mDZP/def2-TZVP level of theory. Structures are classified by the Arg binding mode to Pt.

Figure S6. Comparison of the experimental IRMPD spectrum of $[(Arg–H)PtCl_2]^-$ with theoretical IR spectra predicted for select NN_s binding conformers along with their optimized structures and relative Gibbs energies computed at B3LYP/mDZP/def2-TZVP level of theory at 298 K. Misaligned IR features are highlighted in red.

Figure S7. Comparison of the experimental IRMPD spectrum of $[(Arg–H)PtCl_2]^-$ with theoretical IR spectra predicted for select NO^- binding conformers along with their optimized structures and relative Gibbs energies computed at B3LYP/mDZP/def2-TZVP level of theory at 298 K. Misaligned IR features are highlighted in red.

Figure S8. Comparison of the experimental IRMPD spectrum of $[(Arg–H)PtCl_2]^-$ with theoretical IR spectra predicted for select N_sO^- binding conformers along with their optimized structures and relative Gibbs energies computed at B3LYP/mDZP/def2-TZVP level of theory at 298 K. Misaligned IR features are highlighted in red.

Figure S9. Comparison of the experimental IRMPD spectrum of $[(Arg–H)PtCl_2]^-$ with theoretical IR spectra predicted for select OO^- binding conformers along with their optimized structures and relative Gibbs energies computed at B3LYP/mDZP/def2-TZVP level of theory at 298 K. Misaligned IR features are highlighted in red.

Figure S10. Comparison of the experimental IRMPD spectrum of $[(Arg–H)PtCl_2]^-$ with theoretical IR spectra predicted for select conformers with other side chain binding modes along with their optimized structures and relative Gibbs energies computed at B3LYP/mDZP/def2-TZVP level of theory at 298 K. Misaligned IR features are highlighted in red.

Figure S11. Comparison of the experimental IRMPD spectrum of $[(Arg)PtCl_2+Na]^+$ with theoretical IR spectra predicted for select NN_s binding conformers along with their optimized structures and relative Gibbs energies computed at B3LYP/mDZP/def2-TZVP level of theory at 298 K. Misaligned IR features are highlighted in red.

Figure S12. Comparison of the experimental IRMPD spectrum of $[(Arg)PtCl_2+Na]^+$ with theoretical IR spectra predicted for the NO^- binding conformers along with their optimized structures and relative Gibbs energies computed at B3LYP/mDZP/def2-TZVP level of theory at 298 K. Misaligned IR features are highlighted in red.
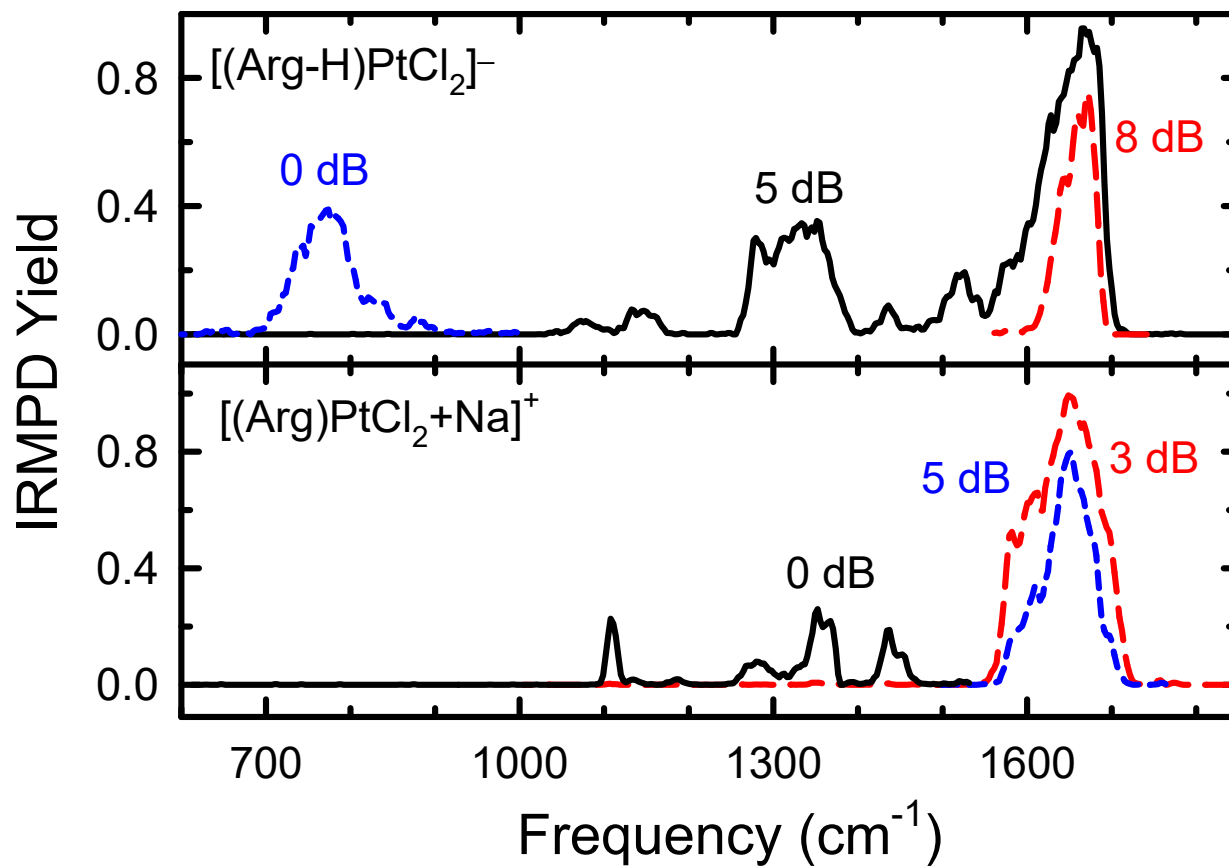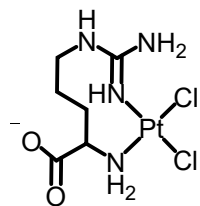
Figure S13. Comparison of the experimental IRMPD spectrum of $[(Arg)PtCl_2+Na]^+$ with theoretical IR spectra predicted for select N_sO binding conformers along with their optimized structures and relative Gibbs energies computed at B3LYP/mDZP/def2-TZVP level of theory at 298 K. Misaligned IR features are highlighted in red.
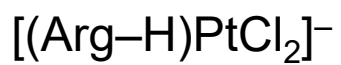
Figure S14. Comparison of the experimental IRMPD spectrum of $[(Arg)PtCl_2+Na]^+$ with theoretical IR spectra predicted for select OO^- binding conformers along with their optimized structures and relative Gibbs energies computed at B3LYP/mDZP/def2-TZVP level of theory at 298 K. Misaligned IR features are highlighted in red.

Figure S15. Comparison of the experimental IRMPD spectrum of $[(Arg)PtCl_2+Na]^+$ with theoretical IR spectra predicted for select conformers with other side chain binding modes along with their optimized structures and relative Gibbs energies computed at B3LYP/mDZP/def2-TZVP level of theory at 298 K. Misaligned IR features are highlighted in red.
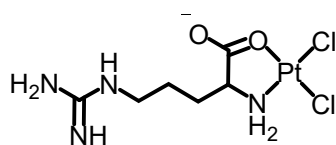
Figure S1.

Figure S2.

$[(Arg–H)PtCl_2]^-$

NN$_s$

NO$^-$

N$_s$O$^-$

OO$^-$

NN$_\omega$

N$_\omega$O$^-$

NN$_\epsilon$

N$_\epsilon$O$^-$

Figure S3.

$$[(Arg)PtCl_2+Na]^+$$
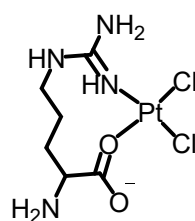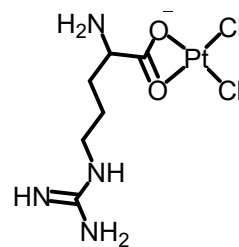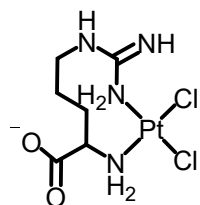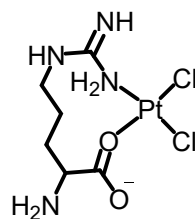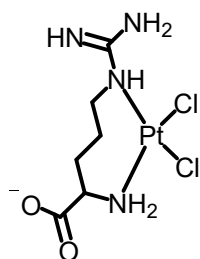
NN$_s$
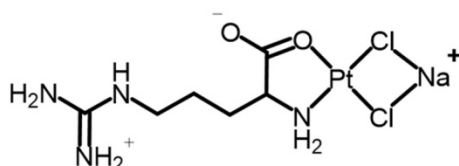
NO$^-$
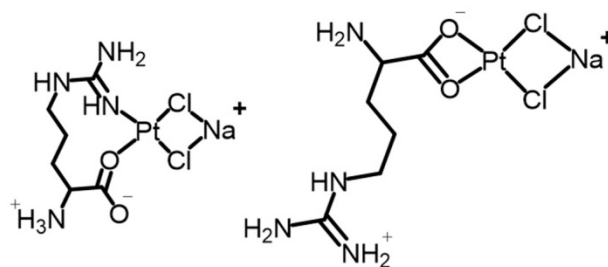
N$_s$O$^-$
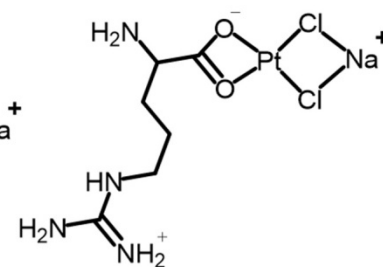
OO$^-$
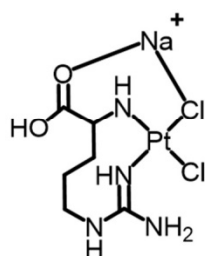
NN$_s$_OCl$_s$
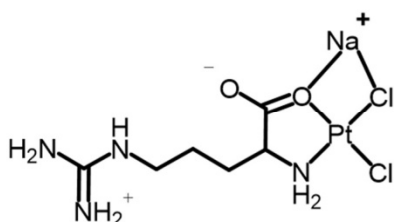
NO$^-$_OCl$_b$

N$_s$O

NN$_s$_OCl$_b$Cl$_s$

NO

N$_s$O$^-$_OCl$_s$

NN$_\varepsilon$

NO_N$_s$Cl$_b$Cl$_O$

N$_\omega$O

NN$_\omega$

N$_\varepsilon$O

Figure S4.

NN$_s$_A
0.0 kJ/mol

NN$_s$_B
7.4 kJ/mol

NN$_s$_C
12.6 kJ/mol

NN$_s$_D
13.1 kJ/mol

NN$_s$_E
14.9 kJ/mol

NN$_s$_F
18.7 kJ/mol

NN$_s$_G
19.4 kJ/mol

NN$_s$_H
28.4 kJ/mol

NN$_s$_I
31.2 kJ/mol

NN$_s$_J
31.5 kJ/mol

NN$_s$_K
33.2 kJ/mol

NN$_s$_L
35.2 kJ/mol

NN$_s$_M
38.3 kJ/mol

NN$_s$_N
40.3 kJ/mol

NN$_s$_O
41.5 kJ/mol

NN$_s$_P
43.0 kJ/mol

NN$_s$_Q
60.6 kJ/mol

NN$_s$_R
66.1 kJ/mol

$[(Arg-H)PtCl_2]^-$, NN$_s$

NO⁻_A
0.0 kJ/mol

NO⁻_B
1.3 kJ/mol

NO⁻_C
1.7 kJ/mol

NO⁻_D
3.5 kJ/mol

NO⁻_E
4.0 kJ/mol

NO⁻_F
5.2 kJ/mol

NO⁻_G
5.2 kJ/mol

NO⁻_H
5.4 kJ/mol

NO⁻_I
6.2 kJ/mol

NO⁻_J
7.2 kJ/mol

NO⁻_K
7.5 kJ/mol

NO⁻_L
7.6 kJ/mol

NO⁻_M
9.8 kJ/mol

NO⁻_N
10.6 kJ/mol

NO⁻_O
11.3 kJ/mol

NO⁻_P
11.6 kJ/mol

NO⁻_Q
11.6 kJ/mol

NO⁻_R
12.3kJ/mol

NO⁻_S
12.5 kJ/mol

NO⁻_T
12.8 kJ/mol

$[(Arg–H)PtCl_2]^-$, NO^-

Figure S4.

NO⁻_U
12.8 kJ/mol

NO⁻_V
13.6 kJ/mol

NO⁻_W
13.9 kJ/mol

NO⁻_X
14.2 kJ/mol

NO⁻_Y
14.2 kJ/mol

NO⁻_Z
14.6 kJ/mol

NO⁻_AA
16.0 kJ/mol

NO⁻_AB
18.0 kJ/mol

NO⁻_AC
18.8 kJ/mol

NO⁻_AD
18.8 kJ/mol

NO⁻_AE
19.1 kJ/mol

NO⁻_AF
19.2 kJ/mol

NO⁻_AG
19.5 kJ/mol

NO⁻_AH
19.7 kJ/mol

NO⁻_AI
19.8 kJ/mol

NO⁻_AJ
19.8 kJ/mol

NO⁻_AK
19.9 kJ/mol

NO⁻_AL
20.5 kJ/mol

NO⁻_AM
20.6 kJ/mol

NO⁻_AN
21.1 kJ/mol

$[(Arg-H)PtCl_2]^-$, NO⁻

Figure S4.

NO⁻_AO
22.7 kJ/mol

NO⁻_AP
23.3 kJ/mol

NO⁻_AQ
23.9 kJ/mol

NO⁻_AR
24.2 kJ/mol

NO⁻_AS
24.3 kJ/mol

NO⁻_AT
24.7 kJ/mol

NO⁻_AU
24.9 kJ/mol

NO⁻_AV
25.1 kJ/mol

NO⁻_AW
25.3 kJ/mol

NO⁻_AX
25.7 kJ/mol

NO⁻_AY
25.9 kJ/mol

NO⁻_AZ
26.0 kJ/mol

NO⁻_BA
26.0 kJ/mol

NO⁻_BB
26.1 kJ/mol

NO⁻_BC
26.1 kJ/mol

NO⁻_BD
26.2 kJ/mol

NO⁻_BE
26.3 kJ/mol

NO⁻_BF
26.7 kJ/mol

NO⁻_BG
27.0 kJ/mol

NO⁻_BH
27.2 kJ/mol

$[(Arg-H)PtCl_2]^-$, NO^-

Figure S4.

NO⁻_BI
27.5 kJ/mol

NO⁻_BJ
27.8 kJ/mol

NO⁻_BK
28.3 kJ/mol

NO⁻_BL
28.6 kJ/mol

NO⁻_BM
28.7 kJ/mol

NO⁻_BN
28.8 kJ/mol

NO⁻_BO
29.3 kJ/mol

NO⁻_BP
30.1 kJ/mol

NO⁻_BQ
30.2 kJ/mol

NO⁻_BR
30.3 kJ/mol

NO⁻_BS
30.8 kJ/mol

NO⁻_BT
31.1 kJ/mol

NO⁻_BU
31.1 kJ/mol

NO⁻_BV
31.1 kJ/mol

NO⁻_BW
31.2 kJ/mol

NO⁻_BX
31.2 kJ/mol

NO⁻_BY
31.3 kJ/mol

NO⁻_BZ
32.6 kJ/mol

NO⁻_CA
33.0 kJ/mol

NO⁻_CB
35.5 kJ/mol

[(Arg–H)PtCl$_2$]⁻, NO⁻

Figure S4.

NO⁻_CC
36.4 kJ/mol

NO⁻_CD
36.5 kJ/mol

NO⁻_CE
36.5 kJ/mol

NO⁻_CF
37.1 kJ/mol

NO⁻_CG
37.7 kJ/mol

NO⁻_CH
38.5 kJ/mol

NO⁻_CI
40.0 kJ/mol

NO⁻_CJ
40.1 kJ/mol

NO⁻_CK
41.3 kJ/mol

NO⁻_CL
44.7 kJ/mol

NO⁻_CM
44.9 kJ/mol

NO⁻_CN
48.1 kJ/mol

$[(Arg–H)PtCl_2]^-$, NO⁻

Figure S4.

N$_s$O$^-$_A
25.1 kJ/mol

N$_s$O$^-$_B
26.2 kJ/mol

N$_s$O$^-$_C
26.9 kJ/mol

N$_s$O$^-$_D
27.0 kJ/mol

N$_s$O$^-$_E
27.4 kJ/mol

N$_s$O$^-$_F
28.1 kJ/mol

N$_s$O$^-$_G
28.6 kJ/mol

N$_s$O$^-$_H
29.0 kJ/mol

N$_s$O$^-$_I
32.9 kJ/mol

N$_s$O$^-$_J
33.4 kJ/mol

N$_s$O$^-$_K
36.4 kJ/mol

N$_s$O$^-$_L
36.7 kJ/mol

N$_s$O$^-$_M
42.1 kJ/mol

N$_s$O$^-$_N
50.8 kJ/mol

N$_s$O$^-$_O
52.4 kJ/mol

N$_s$O$^-$_P
53.8 kJ/mol

N$_s$O$^-$_Q
63.0 kJ/mol

N$_s$O$^-$_R
63.1 kJ/mol

N$_s$O$^-$_S
67.8 kJ/mol

N$_s$O$^-$_T
77.8 kJ/mol

N$_s$O$^-$_U
112.6 kJ/mol

$[(Arg-H)PtCl_2]^-$, N$_s$O$^-$

Figure S4.

OO⁻_A
71.8 kJ/mol

OO⁻_B
74.1 kJ/mol

OO⁻_C
81.7 kJ/mol

OO⁻_D
82.0 kJ/mol

OO⁻_E
83.2 kJ/mol

OO⁻_F
83.7 kJ/mol

OO⁻_G
84.0 kJ/mol

OO⁻_H
84.0 kJ/mol

OO⁻_I
84.9 kJ/mol

OO⁻_J
85.3 kJ/mol

OO⁻_K
87.1 kJ/mol

OO⁻_L
87.5 kJ/mol

OO⁻_M
87.5 kJ/mol

OO⁻_N
87.5 kJ/mol

OO⁻_O
87.7 kJ/mol

OO⁻_P
88.1 kJ/mol

OO⁻_Q
89.0 kJ/mol

OO⁻_R
89.0 kJ/mol

OO⁻_S
89.1 kJ/mol

OO⁻_T
89.5 kJ/mol

$[(Arg–H)PtCl_2]^-$, OO⁻

OO⁻_U
90.8 kJ/mol

OO⁻_V
91.1 kJ/mol

OO⁻_W
91.1 kJ/mol

OO⁻_X
94.3 kJ/mol

OO⁻_Y
95.3 kJ/mol

OO⁻_Z
95.9 kJ/mol

OO⁻_AA
96.8 kJ/mol

OO⁻_AB
103.1 kJ/mol

OO⁻_AC
107.5 kJ/mol

$[(Arg–H)PtCl_2]^-$, OO^-

NN$_\varepsilon$_A
23.9 kJ/mol

NN$_\omega$_A
26.7 kJ/mol

N$_\omega$O⁻_A
32.8 kJ/mol

N$_\varepsilon$O⁻_A
57.2 kJ/mol

$[(Arg–H)PtCl_2]^-$, other side chain binding modes

Figure S5.

NN$_s$_A
0.0 kJ/mol

NN$_s$_B
5.2 kJ/mol

NN$_s$_C
6.3 kJ/mol

NN$_s$_D
7.0 kJ/mol

NN$_s$_E
7.2 kJ/mol

NN$_s$_F
8.6 kJ/mol

NN$_s$_G
11.1 kJ/mol

NN$_s$_H
11.8 kJ/mol

NN$_s$_I
12.2 kJ/mol

NN$_s$_J
13.1 kJ/mol

NN$_s$_K
13.4 kJ/mol

NN$_s$_L
13.7 kJ/mol

NN$_s$_M
14.1 kJ/mol

NN$_s$_N
14.4 kJ/mol

NN$_s$_O
16.4 kJ/mol

NN$_s$_P
17.4 kJ/mol

NN$_s$_Q
18.3 kJ/mol

NN$_s$_R
18.7 kJ/mol

NN$_s$_S
19.9 kJ/mol

NN$_s$_T
20.2 kJ/mol

$[(Arg)PtCl_2+Na]^+$, NN$_s$

Figure S5.

NN$_s$_U
20.3 kJ/mol

NN$_s$_V
20.9 kJ/mol

NN$_s$_W
21.7 kJ/mol

NN$_s$_X
22.1 kJ/mol

NN$_s$_Y
22.6 kJ/mol

NN$_s$_Z
22.9 kJ/mol

NN$_s$_AA
23.5 kJ/mol

NN$_s$_AB
25.5 kJ/mol

NN$_s$_AC
25.5 kJ/mol

NN$_s$_AD
25.6 kJ/mol

NN$_s$_AE
26.6 kJ/mol

NN$_s$_AF
27.0 kJ/mol

NN$_s$_AG
27.1 kJ/mol

NN$_s$_AH
29.3 kJ/mol

NN$_s$_AI
34.1 kJ/mol

NN$_s$_AJ
34.2 kJ/mol

NN$_s$_AK
34.8 kJ/mol

NN$_s$_AL
37.1 kJ/mol

NN$_s$_AM
43.0 kJ/mol

NN$_s$_AN
46.5 kJ/mol

$[(Arg)PtCl_2+Na]^+$, NN$_s$

Figure S5.

NN$_s$_AO
50.1 kJ/mol

NN$_s$_AP
53.7 kJ/mol
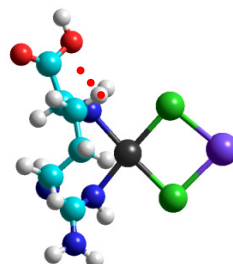
NN$_s$_AQ
58.2 kJ/mol
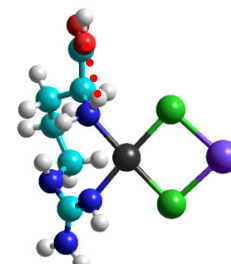
NN$_s$_AR
67.9 kJ/mol

NN$_s$_AS
71.9 kJ/mol

[(Arg)PtCl$_2$+Na]$^+$, NN$_s$

Figure S5.

NO⁻_A
1.8 kJ/mol

NO⁻_B
2.8 kJ/mol

NO⁻_C
7.7 kJ/mol

NO⁻_D
7.8 kJ/mol

NO⁻_E
9.7 kJ/mol

NO⁻_F
11.1 kJ/mol

NO⁻_G
11.6 kJ/mol

NO⁻_H
12.1 kJ/mol

NO⁻_I
12.2 kJ/mol

NO⁻_J
14.0 kJ/mol

NO⁻_K
15.2 kJ/mol

NO⁻_L
17.0 kJ/mol

NO⁻_M
17.5 kJ/mol

NO⁻_N
17.6 kJ/mol

NO⁻_O
18.4 kJ/mol

NO⁻_P
18.6 kJ/mol

NO⁻_Q
19.2 kJ/mol

NO⁻_R
20.0 kJ/mol

NO⁻_S
21.9 kJ/mol

NO⁻_T
24.2 kJ/mol

$[(Arg)PtCl_2+Na]^+$, NO⁻

Figure S5.

NO⁻_U
24.4 kJ/mol

NO⁻_V
25.4 kJ/mol

NO⁻_W
25.8 kJ/mol

NO⁻_X
26.2 kJ/mol

NO⁻_Y
30.7 kJ/mol

NO⁻_Z
33.7 kJ/mol

NO⁻_AA
33.7 kJ/mol

NO⁻_AB
36.5 kJ/mol

NO⁻_AC
40.1 kJ/mol

NO⁻_AD
45.0 kJ/mol

NO⁻_AE
49.9 kJ/mol

NO⁻_AF
60.7 kJ/mol

NO⁻_AG
62.8 kJ/mol

NO⁻_AH
78.7 kJ/mol

NO⁻_AI
79.2 kJ/mol

NO⁻_AJ
85.2 kJ/mol

NO⁻_AK
85.3 kJ/mol

$[(Arg)PtCl_2+Na]^+$, NO⁻

Figure S5.

N$_s$O_A
49.8 kJ/mol

N$_s$O_B
60.1 kJ/mol

N$_s$O_C
61.1 kJ/mol

N$_s$O_D
61.5 kJ/mol

N$_s$O_E
63.6 kJ/mol

N$_s$O_F
64.9 kJ/mol

N$_s$O_G
65.6 kJ/mol

N$_s$O_H
67.3 kJ/mol

N$_s$O_I
69.3 kJ/mol

N$_s$O_J
72.1 kJ/mol

N$_s$O_K
73.3 kJ/mol

N$_s$O_L
73.5 kJ/mol

N$_s$O_M
76.0 kJ/mol

N$_s$O_N
80.0 kJ/mol

N$_s$O_O
81.7 kJ/mol

N$_s$O_P
85.2 kJ/mol

N$_s$O_Q
85.8 kJ/mol

N$_s$O_R
86.4 kJ/mol

N$_s$O_S
92.2 kJ/mol

N$_s$O_T
92.4 kJ/mol

[(Arg)PtCl$_2$+Na]$^+$, N$_s$O

Figure S5.

OO⁻_A
83.1 kJ/mol

OO⁻_B
87.5 kJ/mol

OO⁻_C
88.7 kJ/mol

OO⁻_D
89.4 kJ/mol

OO⁻_E
93.6 kJ/mol

OO⁻_F
94.1 kJ/mol

OO⁻_G
97.7 kJ/mol

OO⁻_H
99 kJ/mol

OO⁻_I
99.9 kJ/mol

OO⁻_J
100.2 kJ/mol

OO⁻_K
100.7 kJ/mol

OO⁻_L
101.9 kJ/mol

OO⁻_M
102.8 kJ/mol

OO⁻_N
102.9 kJ/mol

OO⁻_O
102.9 kJ/mol

OO⁻_P
105.6 kJ/mol

OO⁻_Q
108.2 kJ/mol

OO⁻_R
110.7 kJ/mol

OO⁻_S
111.0 kJ/mol

OO⁻_T
114.5 kJ/mol
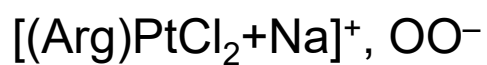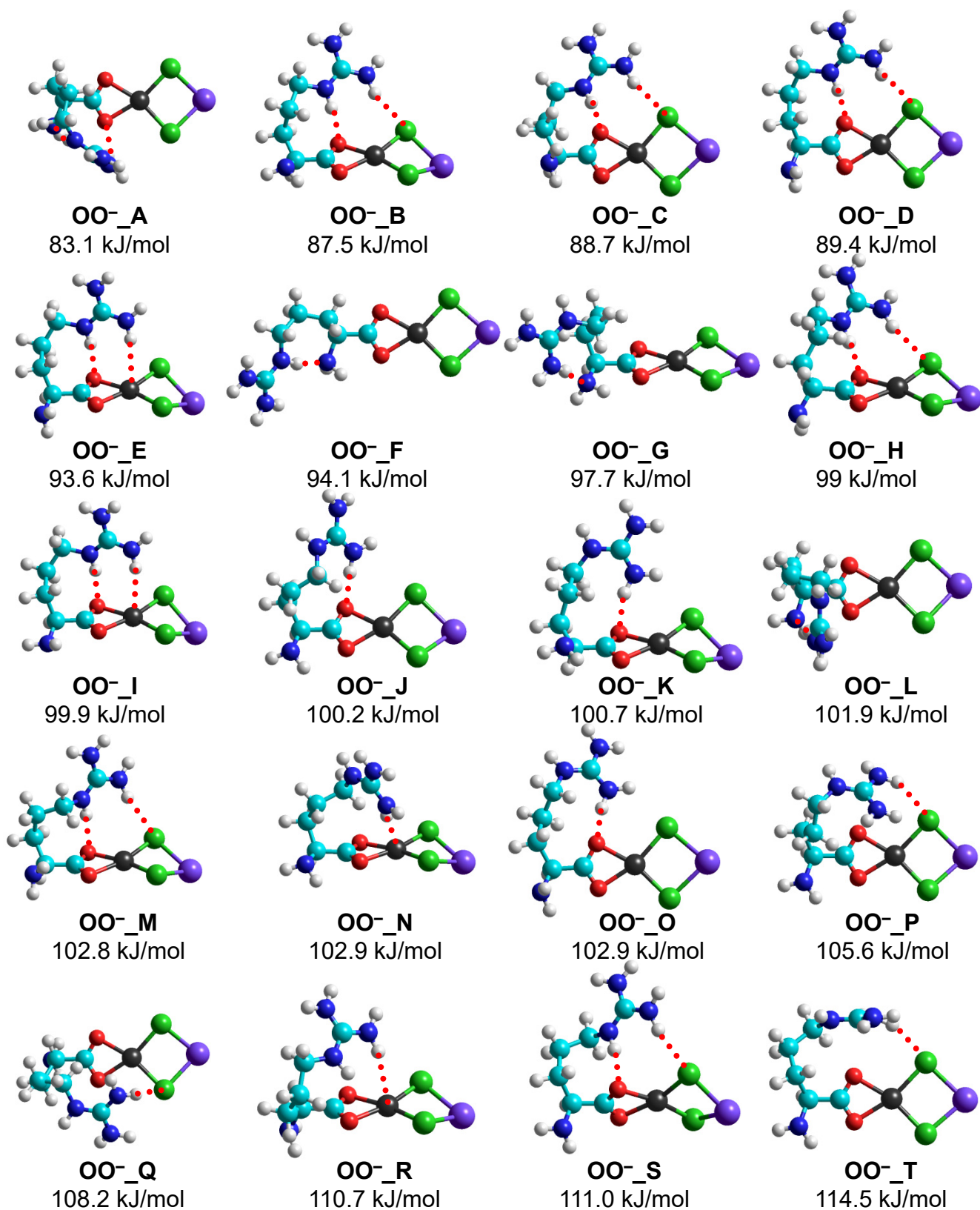
$[(Arg)PtCl_2+Na]^+$, OO⁻
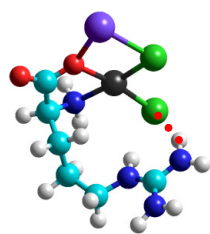
Figure S5.

NO⁻_OCl_b_A
21.4 kJ/mol

NN_s_OCl_bCl_s_A
36.7 kJ/mol
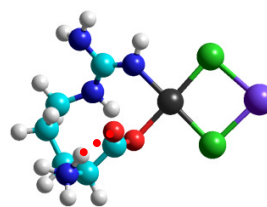
N_sO⁻_A
65.8 kJ/mol
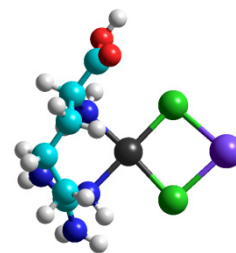
NN_ε_A
67.7 kJ/mol
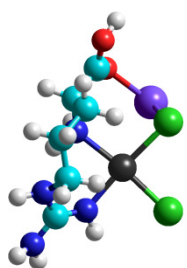
NN_s_OCl_s_A
69.2 kJ/mol
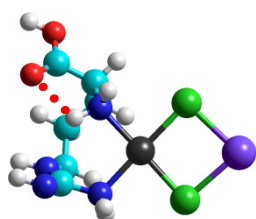
NN_ω_A
80.1 kJ/mol
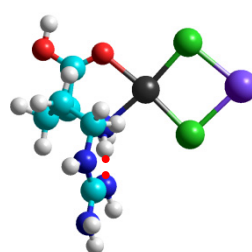
NO_A
84.1 kJ/mol
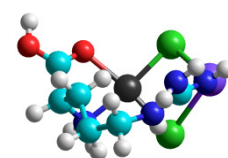
NO_N_sCl_bCl_O_A
86.5 kJ/mol
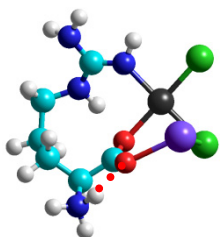
N_sO⁻_OCl_s_A
97.7 kJ/mol
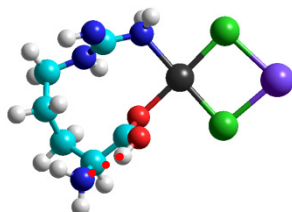
N_ωO_A
121.2 kJ/mol

N_εO_A
145.9 kJ/mol

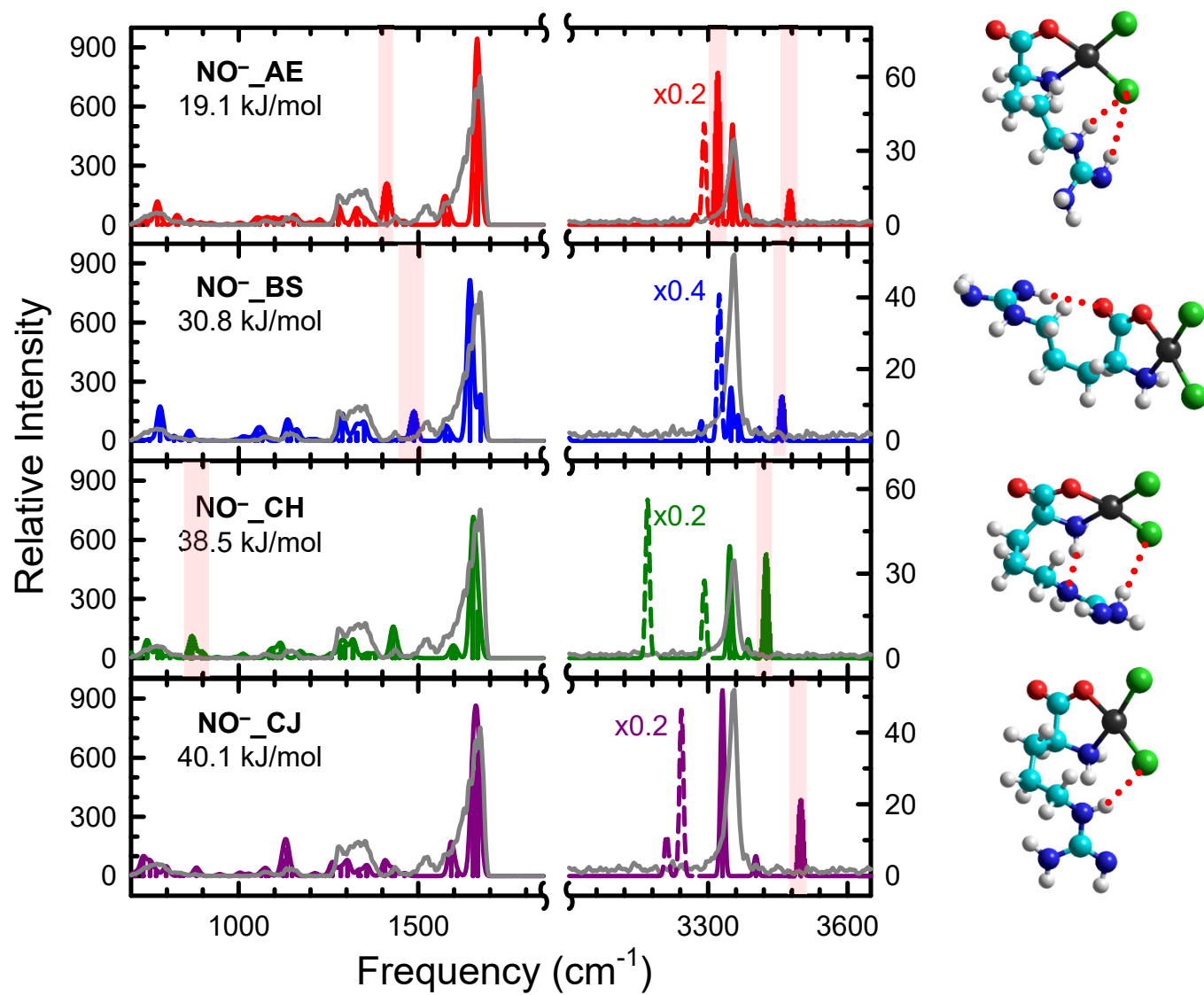$[(Arg)PtCl_2+Na]^+$, Other side chain binding modes

Figure S6.

$[(Arg–H)PtCl_2]^–$, NN$_s$

Figure S7.

NO⁻_B
1.3 kJ/mol
x0.05

NO⁻_F
5.2 kJ/mol
x0.2

NO⁻_W
13.9 kJ/mol

NO⁻_Z
14.6 kJ/mol
x0.1

Relative Intensity

Frequency (cm⁻¹)

$[(Arg–H)PtCl_2]^-$, NO^-

NO⁻_AE
19.1 kJ/mol
x0.2

NO⁻_BS
30.8 kJ/mol
x0.4

NO⁻_CH
38.5 kJ/mol
x0.2

NO⁻_CJ
40.1 kJ/mol
x0.2

Relative Intensity

Frequency (cm⁻¹)

$[(Arg-H)PtCl_2]^-, NO^-$

Figure S8.

$[(Arg-H)PtCl_2]^-$, N_sO^-

Figure S9.

OO⁻_A
71.8 kJ/mol

x0.1

OO⁻_C
81.7 kJ/mol

OO⁻_E
83.2 kJ/mol

x0.2

OO⁻_P
88.1 kJ/mol

x0.1

Relative Intensity

Frequency (cm⁻¹)

$[(Arg–H)PtCl_2]^-$, OO⁻

NN$_\varepsilon$_A
23.9 kJ/mol

NN$_\omega$_A
26.7 kJ/mol

x0.5

N$_\omega$O$^-$_A
32.8 kJ/mol

N$_\varepsilon$O$^-$_A
57.2 kJ/mol

x0.2

Relative Intensity

Frequency (cm^{-1})

[(Arg–H)PtCl$_2$]$^-$, Other side chain binding modes

Figure S11.

$[(Arg)PtCl_2+Na]^+$, NN_s

[(Arg)PtCl$_2$+Na]$^+$, NO$^-$

Figure S13.

$[(Arg)PtCl_2+Na]^+$, N_sO

[(Arg)PtCl$_2$+Na]$^+$, OO$^-$

Figure S15.

NO⁻_OCl_b_A
21.4 kJ/mol

x0.2

NN_s_OCl_bCl_s_A
36.7 kJ/mol

N_sO⁻_A
65.8 kJ/mol

NN_ε___A
67.7 kJ/mol

NN_s_OCl_s_A
69.2 kJ/mol

NN_ω_A
80.1 kJ/mol

Relative Intensity

Frequency (cm⁻¹)

[(Arg)PtCl$_2$+Na]$^+$, Other side chain binding modes

Figure S15.

[(Arg)PtCl$_2$+Na]$^+$, Other side chain binding modes