Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


# Photophysical properties of open-framework germanates templated by nickel complexes

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## SUPPLEMENTARY INFORMATION

**Table S1**. Geometry of the Ni coordination sphere in SUT-1 and SUT-2

| SUT-1 | | SUT-2 | |
|---|---|---|---|
| Bond angle | (°) | Bond angle | (°) |
| *M* = Ni(1) | | | |
| O(18)–*M*–N(2) | 86.83<br>93.34 | O(15)–*M*–N(2) | 89.34<br>90.66 |
| O(18)–*M*–N(1) | 86.23<br>93.60 | O(15)–*M*–N(1) | 92.36<br>87.64 |
| N(1)–*M*–N(1) | 83.89 | N(1)–*M*–N(2) | 82.91<br>97.09 |
| N(1)–*M*–N(2) | 96.01 | | |
| N(2)–*M*–N(2) | 84.08 | | |
| *M* = Ni(2) | | | |
| N(3)–*M*–N(4) | 86.69 | N(3)–*M*–N(4) | 97.15<br>82.85 |
| N(4)–*M*–N(6) | 92.05 | | |
| N(6)–*M*–N(5) | 87.42 | O(38)–*M*–N(3) | 85.27<br>94.73 |
| N(5)–*M*–N(3) | 93.86 | | |
| | | O(38)–*M*–N(4) | 91.35<br>88.65 |

**Table S2**. Initialization of the Ni spins in the SIESTA simulations

| Atom | Symmetry | Coordinates | | | Spin ($\mu_B$) |
|---|---|---|---|---|---|
| SUT-1 | | | | | |
| Ni(1) | $x, y, z$ | 0.50128 | 0 | ¾ | –2 |
| Ni(1) | $½ + x, ½ + y, ½ – z$ | 0.00128 | ½ | ¾ | –2 |
| Ni(1) | $–x, –y, –z$ | 0.49872 | 0 | ¼ | +2 |
| Ni(1) | $½ – x, ½ – y, ½ + z$ | 0.99872 | ½ | ¼ | +2 |
| SUT-2 | | | | | |
| Ni(2) | $x, y, z$ | ½ | 0 | ½ | –2 |
| Ni(1) | $½ – x, ½ + y, ½ – z$ | 0 | ½ | ½ | –2 |
| Ni(1) | $x, y, z$ | ½ | 0 | 0 | +2 |
| Ni(2) | $½ – x, ½ + y, ½ – z$ | 0 | ½ | 0 | +2 |

**Table S3.** Ni orbital occupancy in the SUT germanates and molecular complexes

| Transition metal | Occupancy | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | *s* | *p* | $d_{xy}$ | $d_{yz}$ | $d_{3z^2-r^2}$ | $d_{xz}$ | $d_{x^2-y^2}$ | Total |
| SUT-1 | | | | | | | | |
| Ni(1)↑ | 0.13 | 3.11 | 0.92 | 0.92 | 0.95 | 0.92 | 0.97 | 7.93 |
| Ni(1)↓ | 0.11 | 3.11 | 0.91 | 0.88 | 0.16 | 0.91 | 0.28 | 6.36 |
| Ni(2) | 0.34 | 6.27 | 1.83 | 1.82 | 1.71 | 1.82 | 0.82 | 14.62 |
| SUT-2 | | | | | | | | |
| Ni(1)↑ | 0.12 | 3.10 | 0.92 | 0.93 | 0.95 | 0.93 | 0.97 | 7.92 |
| Ni(1)↓ | 0.11 | 3.10 | 0.88 | 0.80 | 0.26 | 0.82 | 0.34 | 6.31 |
| Ni(2)↑ | 0.12 | 3.09 | 0.92 | 0.93 | 0.95 | 0.93 | 0.97 | 7.91 |
| Ni(2)↓ | 0.11 | 3.09 | 0.89 | 0.92 | 0.16 | 0.90 | 0.28 | 6.35 |
| $[Ni(en)_3](NO_3)_2$ | | | | | | | | |
| Ni(1)↑ | 0.12 | 6.22 | 0.92 | 0.92 | 0.97 | 0.92 | 0.97 | 11.04 |
| Ni(1)↓ | 0.11 | 3.11 | 0.91 | 0.91 | 0.22 | 0.91 | 0.22 | 6.39 |
| $[Ni(C_4H_{10}N_5)_2]$ | | | | | | | | |
| Ni(1) | 0.34 | 6.33 | 1.83 | 1.79 | 1.71 | 1.79 | 0.83 | 14.62 |

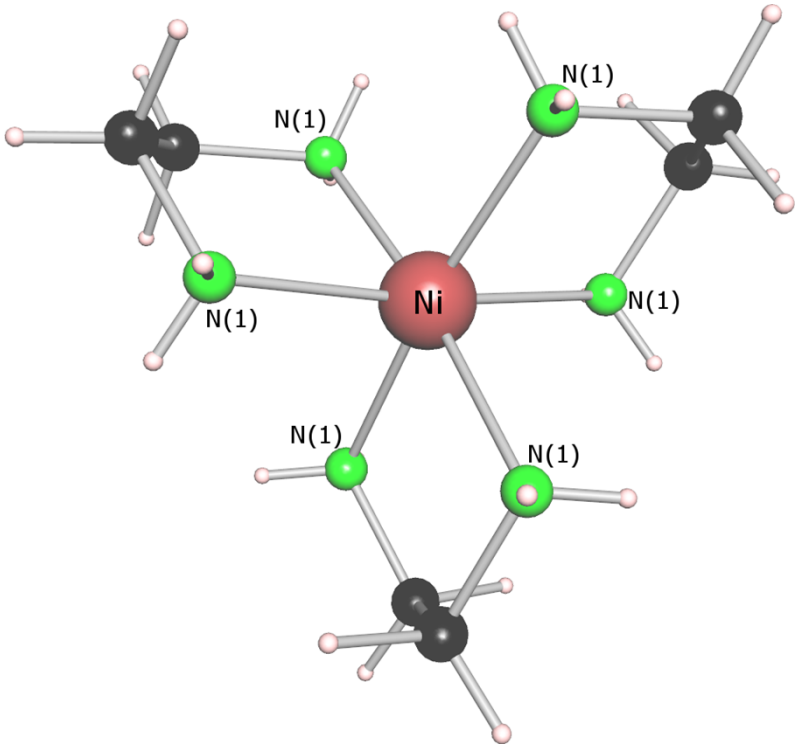


**Figure S1**. Molecular structure of the $[Ni(en)_3]^{+2}$ complex.

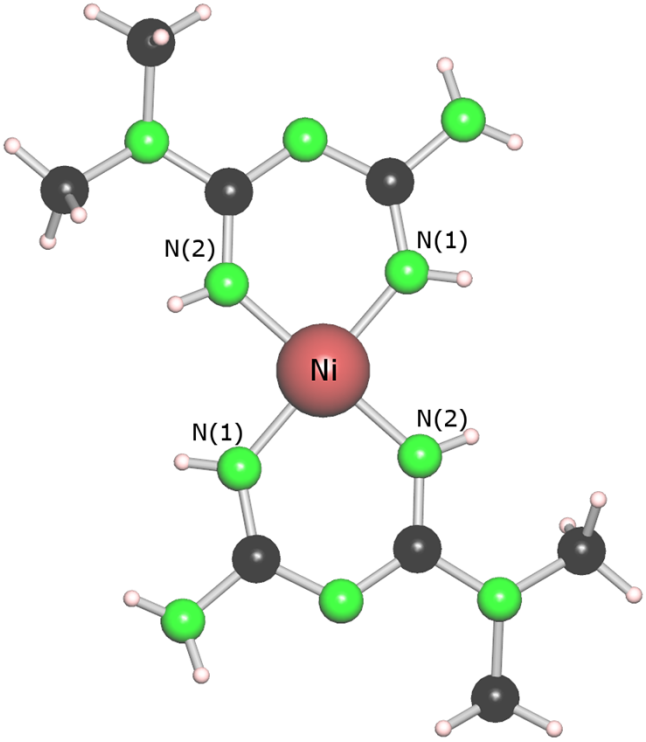


**Figure S2**. Molecular structure of the $[Ni(C_4H_{10}N_5)_2]$ complex.

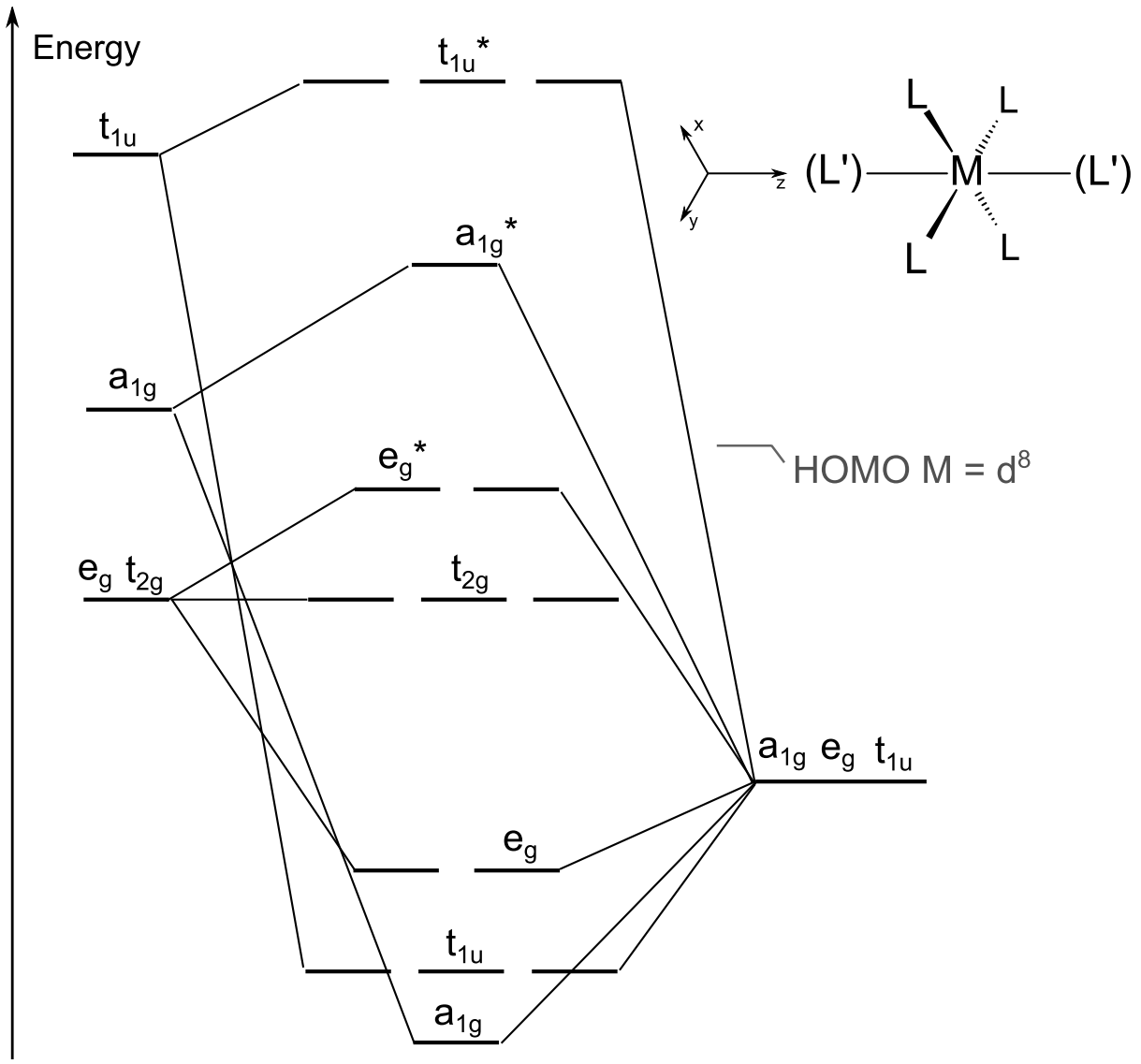


**Figure S3**. Molecular orbital diagram for a sigma-bonded octahedral complex [1].

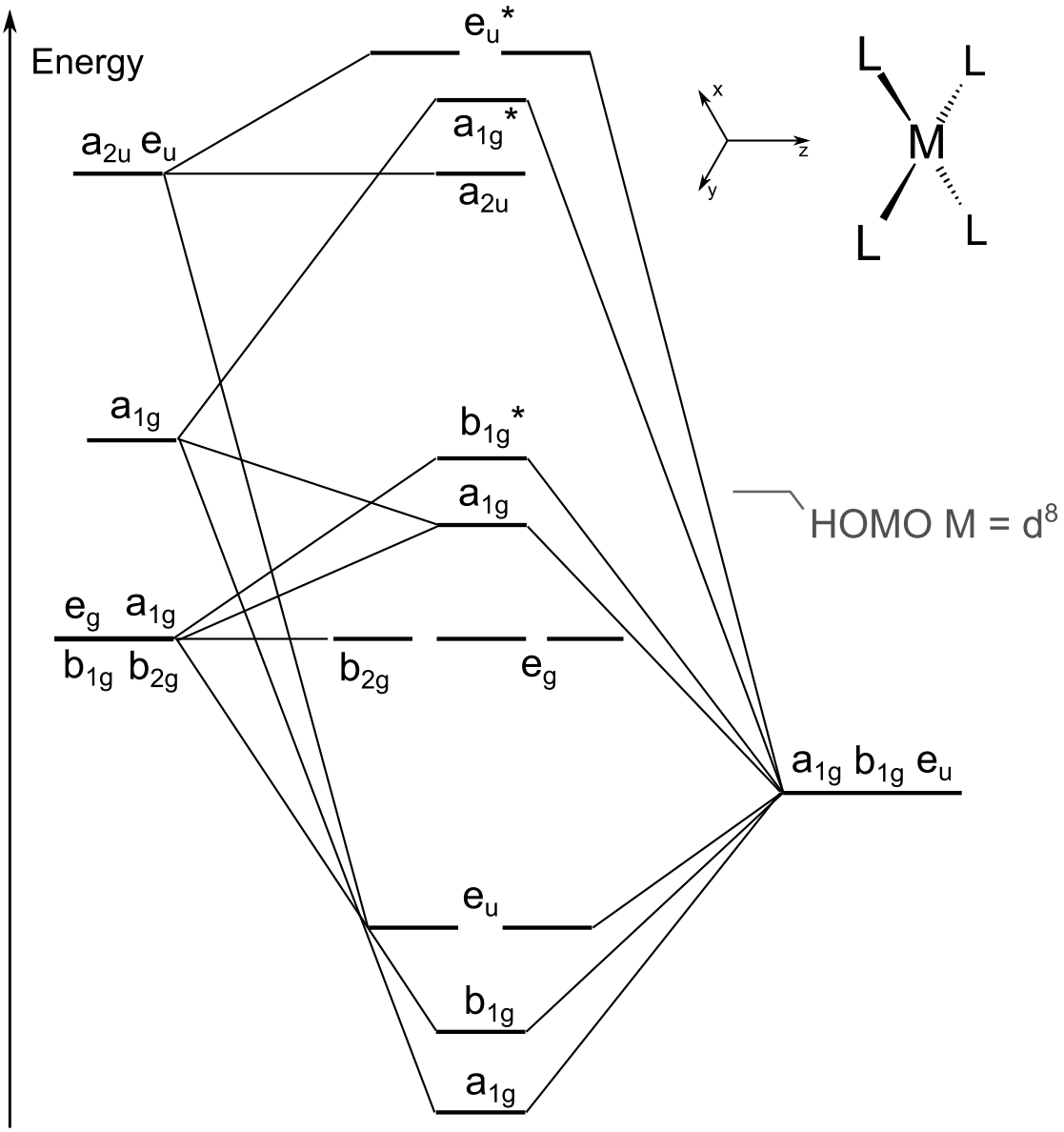


**Figure S4**. Molecular orbital diagram for a sigma-bonded square planar complex [1].

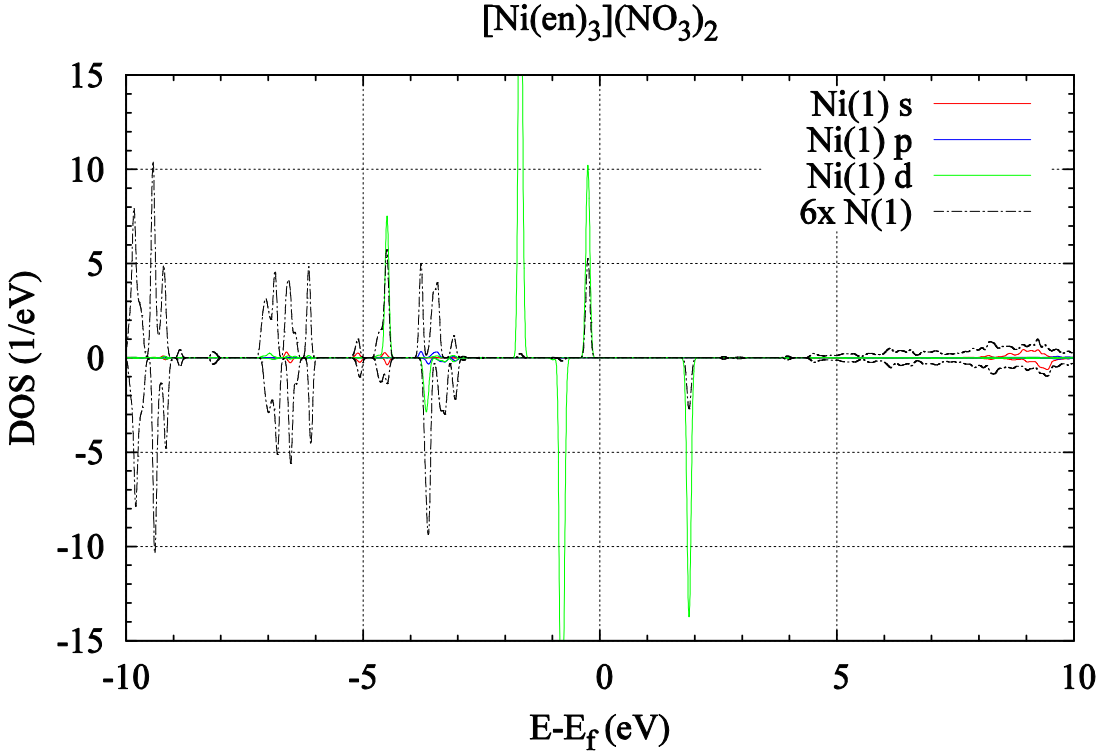


**Figure S5**. DOS of the six N atoms linked to Ni in the complex $[Ni(en)_3](NO_3)_2$.

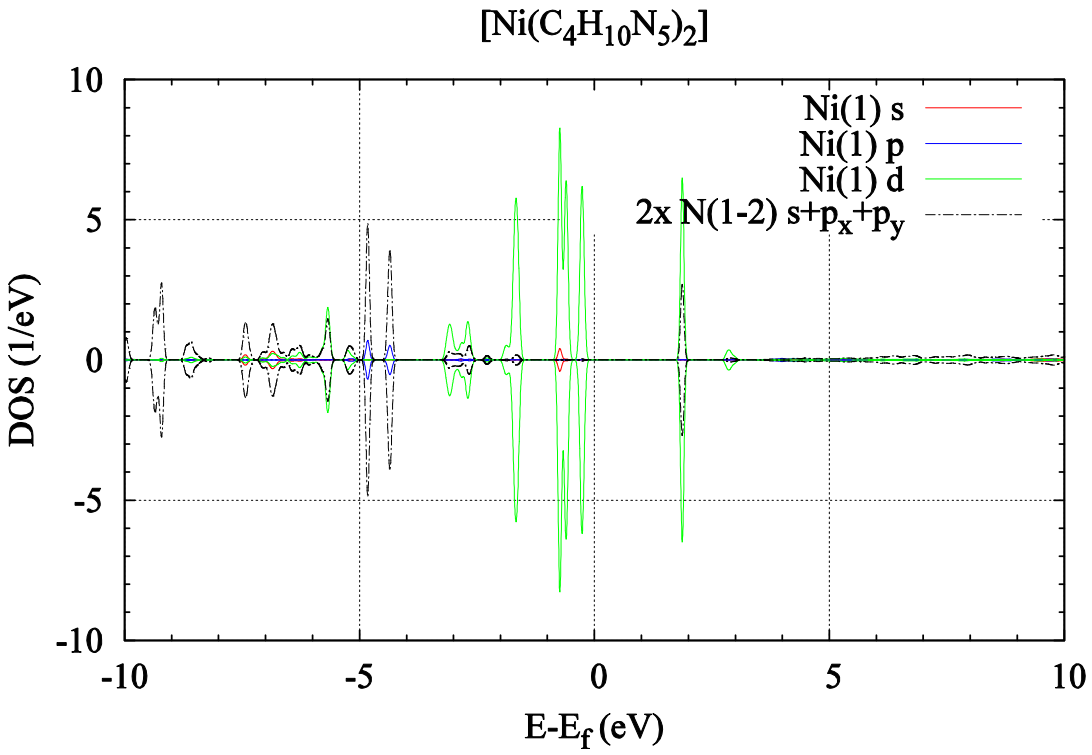


**Figure S6**. DOS of the four N atoms linked to Ni in the complex $[Ni(C_4H_{10}N_5)_2]$.

## References

1. J. E. Huheey, E. A. Keiter, R. L. Keiter, *Inorganic Chemistry*. *Principles of Structure and Reactivity*, 4th ed., HarperColins, 1993.