

Electronic supporting information:

Determination of the Nature of the Cu Coordination Complexes Formed in the Presence of NO and NH₃ within SSZ-13

Ines Lezcano-Gonzalez,^{a,b} David S. Wragg^c, Wojciech. A. Slawinski^c, Karen Hemelsoet^d, Andy Van Yperen-De Deyne^d, Michiel Waroquier^d, Veronique Van Speybroeck^d and Andrew M. Beale^{*a,b}

^aDepartment of Chemistry, University College London, 20 Gordon Street, WC1H 0AJ, London, UK

^bUK Catalysis Hub, Rutherford Appleton Laboratory, Research Complex at Harwell, Didcot, OX11 0FA, UK

^cINGAP Centre for Research Based Innovation, Department of Chemistry, University of Oslo, N-0315 Oslo, Norway

^dCenter for Molecular Modelling (CMM), Ghent University, Technologiepark 903, B-9052, Zwijnaarde, Belgium; QCMM-alliance, Ghent-Brussels, Belgium

*E-mail to: andrew.beale@ucl.ac.uk

1. NO exposure (Cu-SSZ-13-NO)

1.1. PD

Table S1. Rietveld refinement details and results

Radiation, Wavelength (Å)	SNBL beamline BM01A, 0.69811
Crystal System	Trigonal (hexagonal axes)
Space Group	R-3m (No.166)
<i>a</i> , <i>c</i> (Å), volume (Å ³)	13.5717(3), 14.7653(4), 2355.3(1)
Rwp, Rp, Rexp	2.713, 4.020, 0.190
Rwp, Rp, Rexp - background	7.403, 6.032, 0.518
R Bragg	3.37
GooF	14.289
Parameters	38
Restraints	0
Constraints	9
Number of Data Points	1554

Table S2. Atomic coordinates, thermal parameters and site occupancies

Atom	x	y	z	B(eq)(Å ²)	Site Occupancy
Si1	-0.0002(2)	0.2283(2)	0.1043(1)	0.01(4)	1
O1	0.9009(2)	0.0991(3)	0.1233(5)	0.67(6)*	1
O2	0.6473(4)	0.6473(4)	1/2	0.67(6)*	1
O3	0.1206(3)	0.2412(5)	0.1318(4)	0.67(6)*	1
O4	0	0.2641(4)	0	0.67(6)*	1
Cu1	1/2	1/2	0	0.2	0.033(4)
O5	0.60971	0.21942	0.73458	1.00(9)†	0.076(7)‡
N2	0.99962	0.82852	0.60961	1.00(9)†	0.076(7)‡
Ophys	0.34347	0.67173	0.31188	1.00(9)†	0.022(6)
Ophys	0.53207	0.26603	0.59386	1.00(9)†	0.028(3)
N1	0.53068	0.76534	0.23482	1.00(9)†	0.13(2)

* constrained to same B(eq) value for all framework oxygen; † constrained to 1.5 times the Beq of the framework oxygen atoms; ‡ both the atoms of the NO molecule were constrained to the same site occupancy.

Table S3. Bond lengths and angles (selected)

Atoms	Bond length (Å)	Atoms	Bond Angle (°)
Si1-O1	1.613(3)	O3-Si1-O4	110.9(3)
Si1-O2	1.603(3)	O1-Si1-O3	108.8(3)
Si1-O3	1.611(4)	O2-Si1-O3	107.6(3)
Si1-O4	1.611(2)	Si1-O3-Si1	148.1(5)
Cu1-O3	3.167(6)	Si1-O4-Si1	148.8(4)
Cu1-N2	2.38	O3-Cu1-N1	67.7(1)
Cu1-N1	2.16	O3-Cu1-N2	86.6(1)
O5-N2	1.36	O2-Cu1-N1	64.4(1)
		O2-Cu1-N2	82.1(2)
		Cu1-N2-O5	146.7

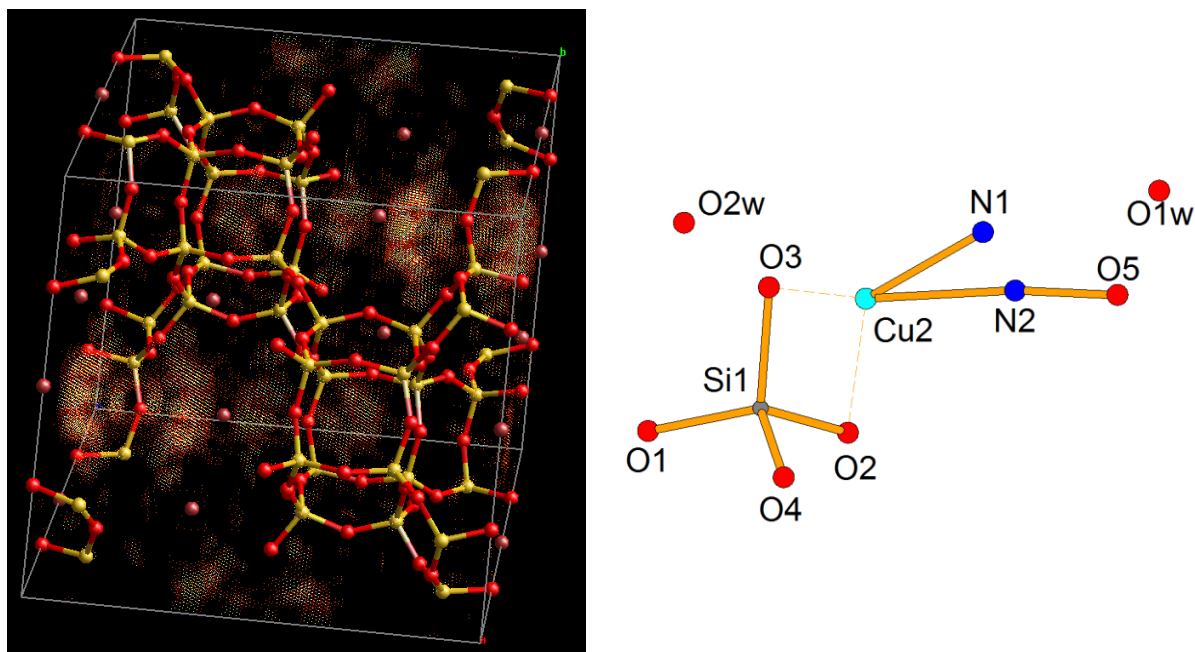


Figure S1. Difference Fourier map upon NO exposure (left), and asymmetric unit of the crystal structure model for SSZ-13 containing adsorbed NO (right).

1.2. Computational details

The obtained NO distance equals 1.15 Å, which is only slightly smaller compared to the 1.17 Å distance of a gas phase $\text{N}\equiv\text{O}$ radical (calculated using the same theoretical methodology). The theoretically obtained closest Cu-O distance is in good agreement with the experimental one. This is also the case for the closest Cu-T distance (Cu-T1, with T a general tetrahedral atom, either Si or Al). The agreement between theory and experiment for the distance between the Cu ion and the other T atoms (Cu-T2, with T2 all Si atoms) is still reasonable, although somewhat less good. This is due to the rather flexible behavior of the Si-O-Si parts of the zeolitic framework allowing the Si atoms to move further or closer to the metal cation.

From Figure S2, it is clear that the position of the Cu ion determines the Cu-N distance and the obtained angle between the adsorbed NO molecule and the Cu ion.

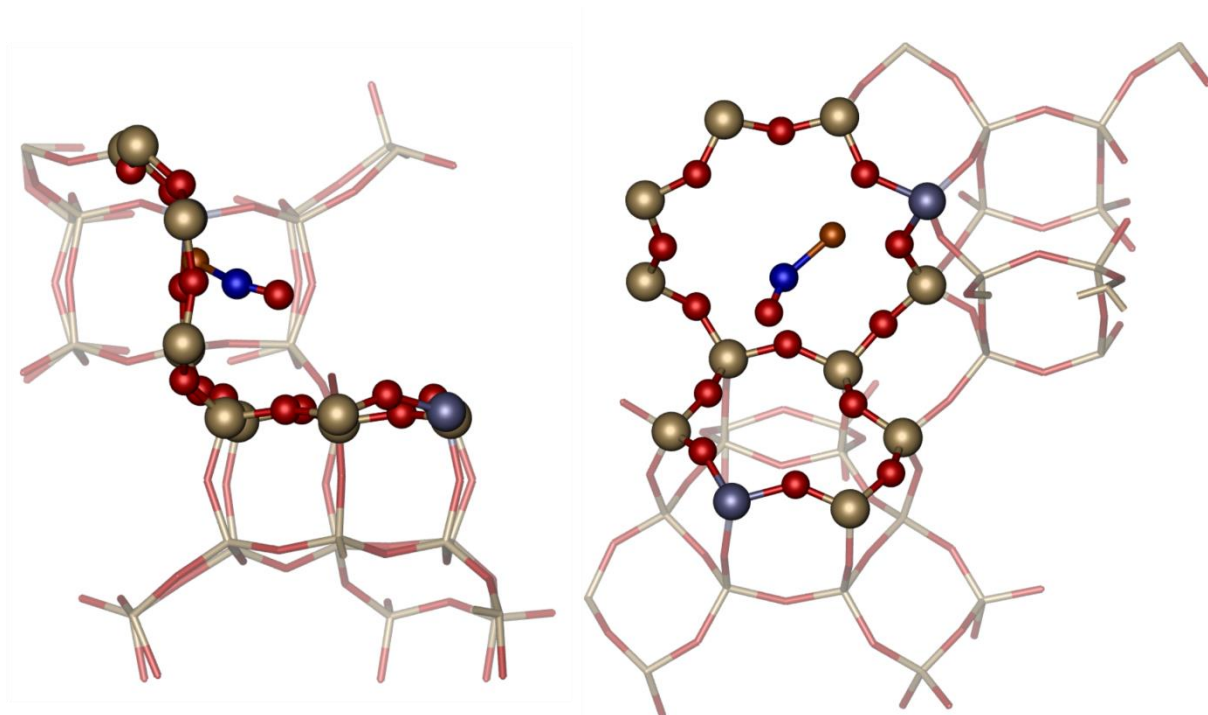


Figure S2. Different views of the optimized Cu-NO nitrosyl complex formed in SSZ-13 using periodic PBE-D3 simulations, with the copper initially in the 8r.

From the MD trajectories, the mobility of the copper ion and the copper center after NO adsorption can be investigated. As a measure of this mobility, the variation of the copper ion location – relative to the averaged MD position- is listed in Table S4 for the various situations. From Table S4 it can be seen that the copper ion remains relatively located in the 8r window. Figures S3 and S4 also reveal that NO adsorption enhances the mobility of the copper ion, the effect being larger in case of adsorption near the 6r as compared to adsorption near the 8r. Analysis of the distances between the Cu ion and the planes of the 6r and 8r along the MD trajectories indicates that during the 10 ps MD simulations the copper ions move around in a range of approximately 1 Å, both in a vertical and horizontal direction (see Figure S4). The difference in mobility between the bare copper ions and those after adsorption of a NO molecule is very small.

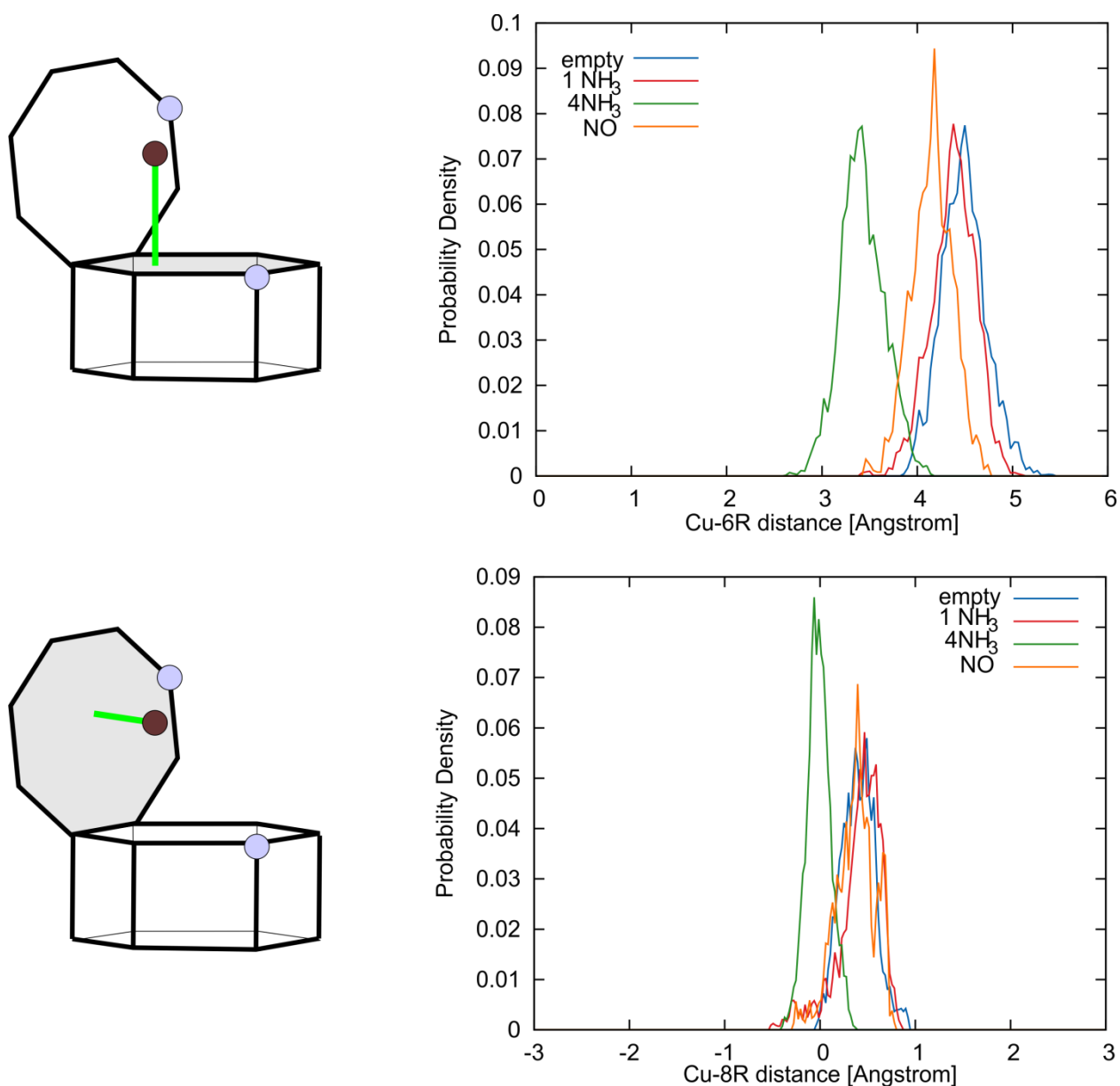


Figure S3. Probability of the distance between the **copper ion originally located near the 8r** and the plane of the 6r (top) and 8r window (bottom) in case of parent model (blue curve), NO@Cu (orange curve), NH₃@Cu (red curve) and [Cu(NH₃)₄]²⁺ (green curve).

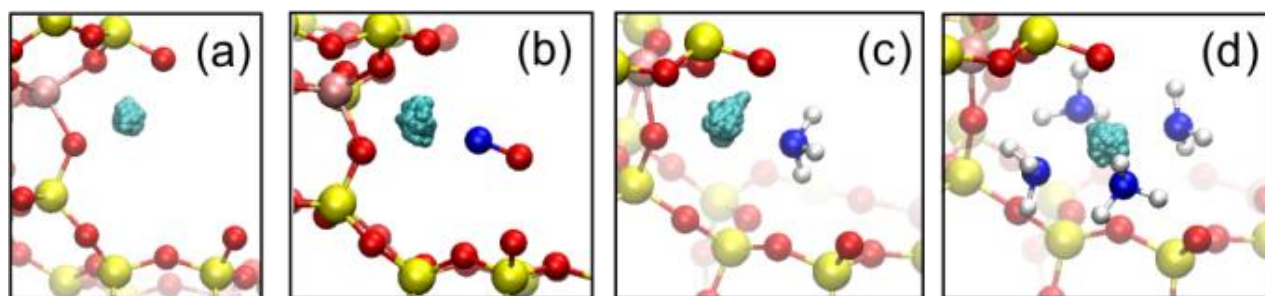


Figure S4. Representation of locations of the **copper ion originally located near the 8r** during the MD runs at 300 K. In case of (a) parent Cu-SSZ-13 model, (b) NO adsorption, (c) NH₃ adsorption and (d) formation of [Cu(NH₃)₄]²⁺.

Table S4. Standard variation σ of the Cu location for the parent and NO and NH₃-adsorbed complexes. Computed from the 10 ps MD runs at 300 K.

	parent	NO@Cu	NH ₃ @Cu	(NH ₃) ₄ @Cu
Cu near 8r	0.20	0.22	0.29	0.24

2. NH₃ exposure (Cu-SSZ-13-NH₃)

2.1. PD

Table S5. Rietveld refinement details and results

Radiation, Wavelength (Å)	SNBL beamline BM01A, 0.69811
Crystal System	Trigonal (hexagonal axes)
Space Group	R-3m (No.166)
<i>a</i> , <i>c</i> (Å), volume (Å ³)	13.5731(2), 14.7607(3), 2355.01(10)
Rwp, Rp, Rexp	4.878, 7.951, 0.203
Rwp, Rp, Rexp - background	11.508, 14.250, 0.480
R Bragg	8.78
GooF	23.988
Parameters	33
Restraints	0
Constraints	6
Number of Data Points	1554

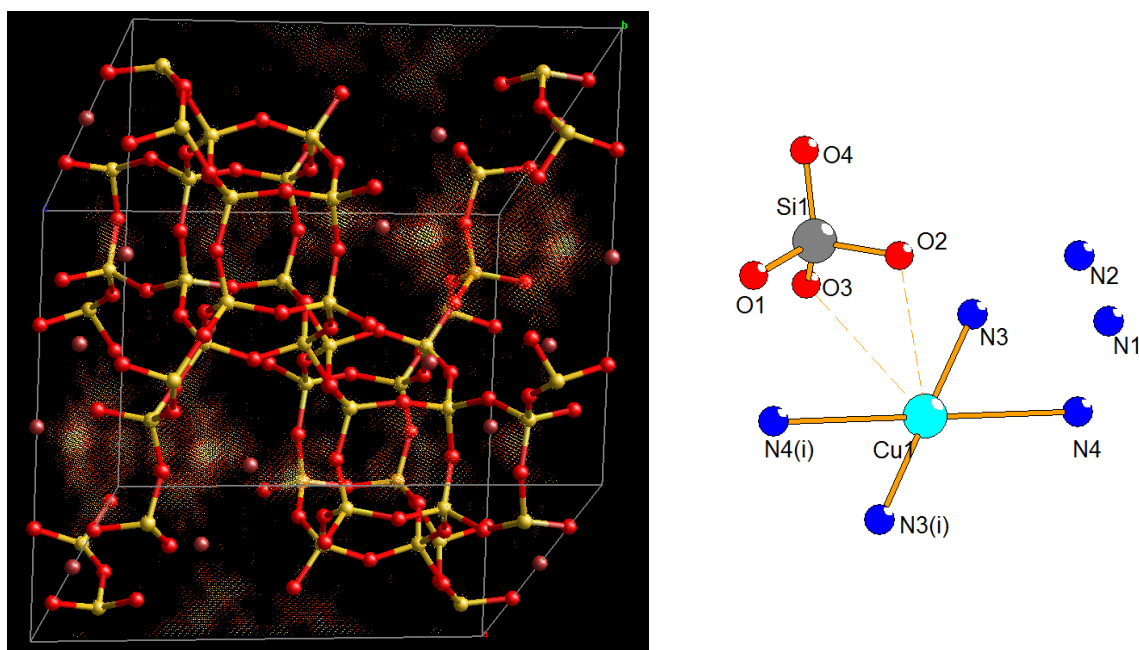
Table S6. Atomic coordinates, thermal parameters and site occupancies

Atom	x	y	z	B(eq)[Å ²]	Occ
Si1	0.00021(17)	0.22849(12)	0.10442(8)	0.10(2)	1
O1	0.90055(17)	0.09945(17)	0.1258(3)	0.75(4)*	1
O2	0.6493(3)	0.6493(3)	1/2	0.75(4)*	1
O3	0.12056(18)	0.2411(4)	0.1324(3)	0.75(4)*	1
O4	0	0.2636(3)	0	0.75(4)*	1
Cu2	1/2	1/2	0	1.125(6)†	0.034(2)
N1	0.34336	0.67168	0.29743	1.125(6)†	0.086(6)
N2	1	1	0.45520	1.125(6)†	0.08(2)
N3	0.53058	0.76529	0.23489	1.125(6)†	0.18(1)
N4	0.56292	0.28146	0.60991	1.125(6)†	0.12(1)

See footnotes to table in 1.1 section of the SI

Table S7. Bond lengths and angles (selected)

Atoms	Bond length (Å)	Atoms	Bond Angle (°)
Si1-O3	1.609(4)	O2-Si1-O3	107.0(2)
Si1-O4	1.6137(16)	O1-Si1-O4	112.4(2)
Si1-O1	1.621(3)	O1-Si1-O2	109.5(2)
Si1-O2	1.610(4)	Si1-O3-Si1	148.4(3)
Cu1-N3	2.16	Si1-O4-Si1	145.6(2)
Cu1-N4	2.83	O3-Cu1-N3	67.83(8)
Cu1-O3	3.157(4)	O3-Cu1-N4	127.32(7)

**Figure S5.** Difference Fourier map upon NH_3 exposure (left), and asymmetric unit of the crystal structure model for SSZ-13 containing adsorbed NH_3 (right). Dotted bonds indicate the shortest O-Cu contacts. N3(i) and N4(i) are symmetry equivalents of the atoms N3 and N4.

2.2. Computational details

Adsorption of up to four ammonia molecules to Cu^{2+} (originally located in the 8r) was simulated using periodic simulations employing PBE-D3. The resulting structures are given in Figure S6. In case of two ammonia molecules, this results in a non-linear geometry for the $[\text{Cu}(\text{NH}_3)_2]^{2+}$ complex, the obtained N-Cu-N angle equals 99° – as opposed to the linear structure recently proposed by Giordanino et al. [1]. However, attempts to optimize such a linear structure were not successful, and no stable linear geometry could be found. The Cu ion tends to coordinate with 2 NH_3 molecules and 2 framework oxygen atoms, as illustrated in Figure S6. In case of four ammonia molecules, the Cu-amine $[\text{Cu}(\text{NH}_3)_4]^{2+}$ complex has a computed average Cu-N bond length of 2.04 Å which compares very well with experiment.

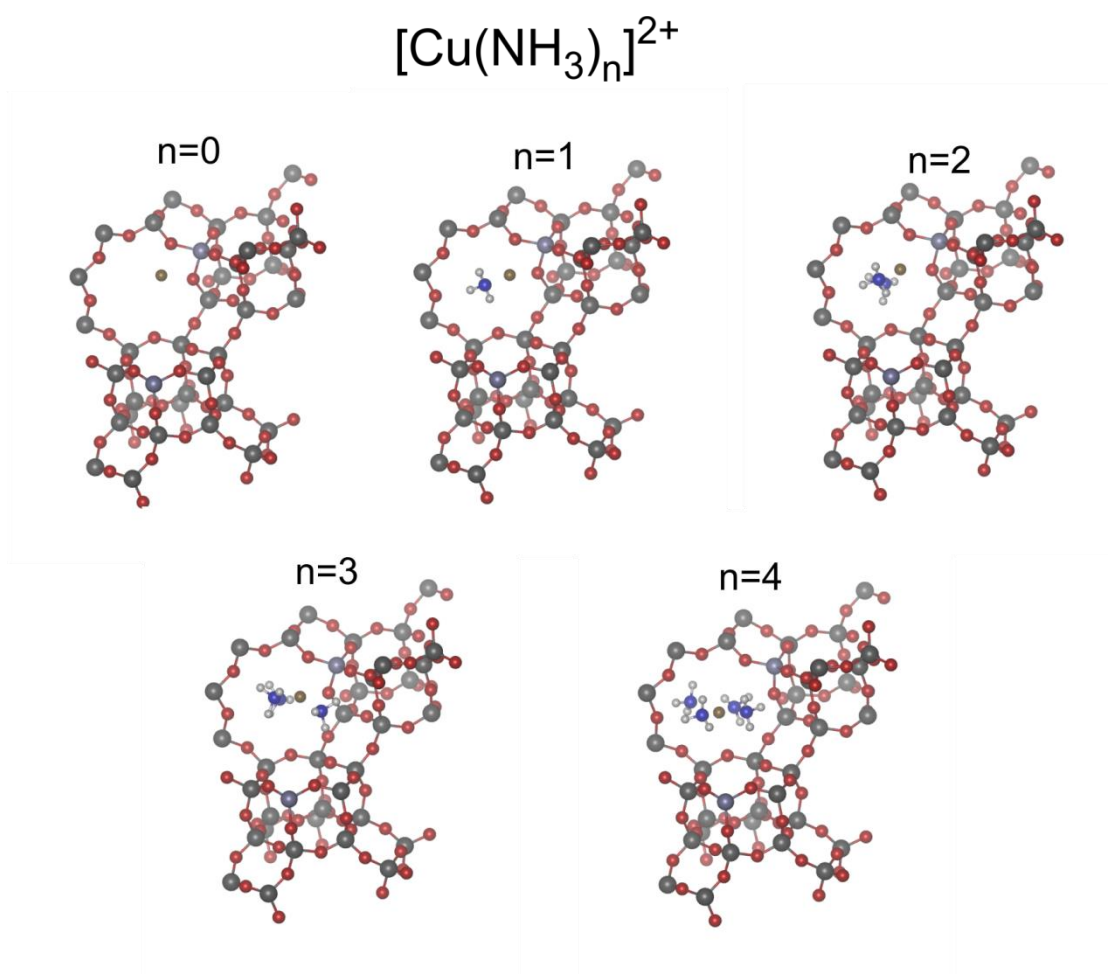


Figure S6. Optimized Cu-ammonia complexes $[\text{Cu}(\text{NH}_3)_n]^{2+}$, as a function of increasing ammonia content, formed in SSZ-13 using periodic PBE-D3 simulations, with the copper initially in the 8r.

For this $[\text{Cu}(\text{NH}_3)_4]^{2+}$ complex, another configuration was previously obtained with the Cu-complex in the center of the *cha* cage. For this structure, the addition of an extra water molecule results in a distorted square-pyramidal structure, as shown in Fig. S7.

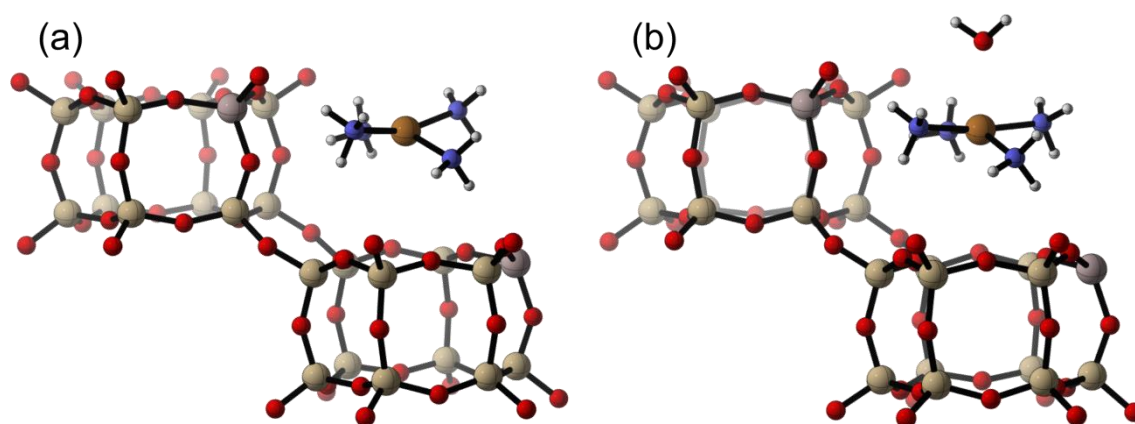


Figure S7. Optimized $[\text{Cu}(\text{NH}_3)_4]^{2+}$ and $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})]^{2+}$.

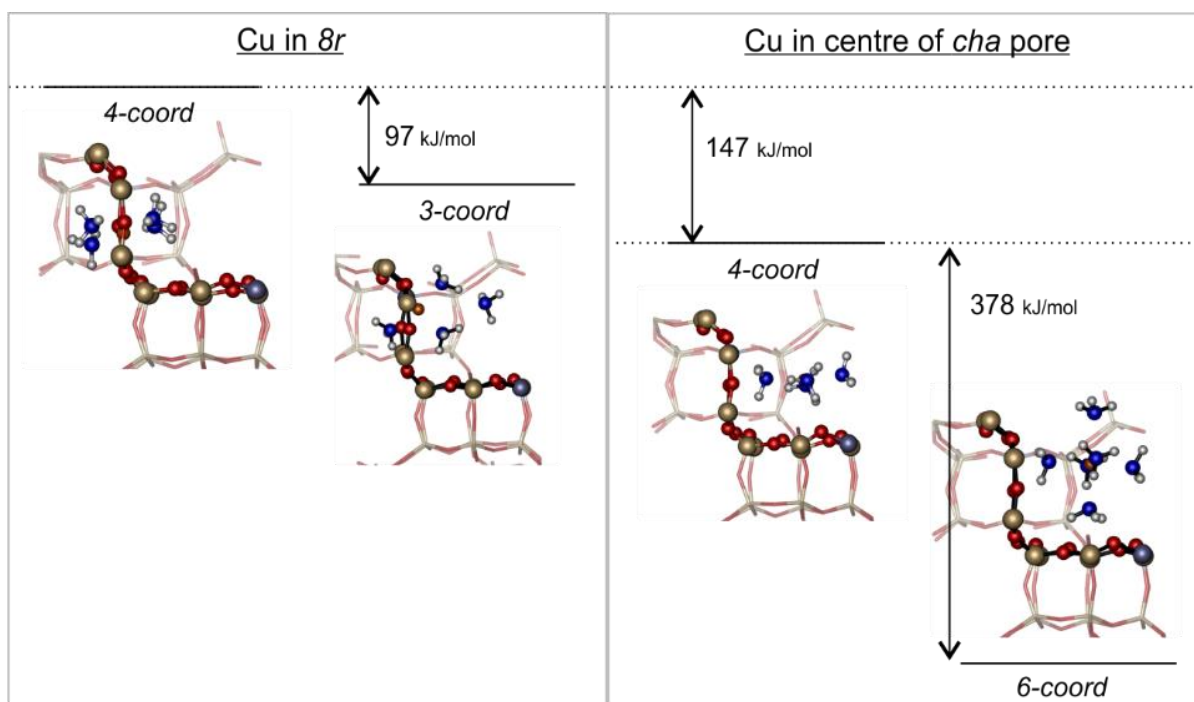


Figure S8. Relative stability plot for four different Cu amine complexes.

References

[1] F. Giordanino, E. Borfecchia, K. A. Lomachenko, A. Lazzarini, G. Agostini, E. Gallo, A. V. Soldatov, P. Beato, S. Bordiga, C. Lamberti, J. Phys. Chem. Lett. 5 (2014) 1552.

Note

Copies of the raw PD, normalized XANES and fitted EXAFS data can be found at the following:
<http://tiny.cc/ACSJPCC5b06875>