Cross-investigation on copper nitroprusside: combining XRD and XAS for in-depth structural insights

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Supplementary Information

Figure S1 reports the Pawley refinement on the hydrated structure with *P2/m* space group in case of an isotropic or generalized µstrain model. In both cases the fit appears very satisfying and the insets displaying the *(11-2)*, *(21-1)*, *(022)*, and *(220)* reflections show a good match with the experimental pattern, although the residual curve derived from the adopted generalized model is slightly flatter as shown for the *(11-2)* and *(21-1)* reflections as well as the global fit goodness parameter ($R_{wp}^{isotropic}$ = 5.462%; $R_{wp}^{generalized}$ = 5.315 %).

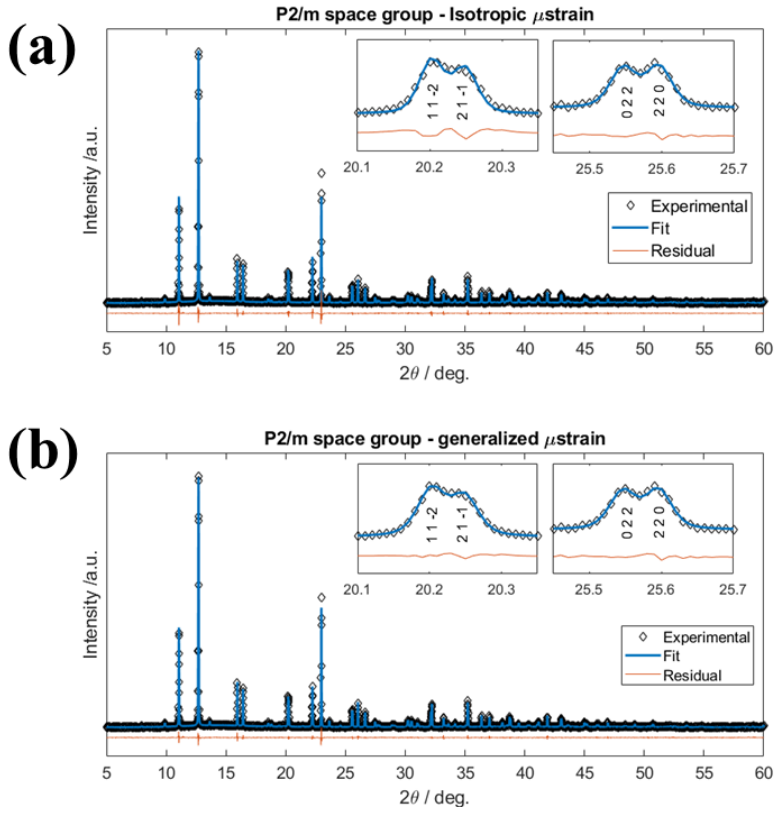

Figure S1. Pawley refinement on the hydrated structure with *P2/m* space group. Panel **(a)** diplays the fit conducted by considering an isotropic µstrain model, while a generalized µstrain model was adopted in the refinement shown in panel **(b)**.

The adoption of the generalized μstrain model is justified in **Figure S2** and it is related with the different peak shape of certain reflections. For instance, the *(20-2)* reflection appears broader than the *(121)* one and they are better fitted by considering a generalized μstrain model.

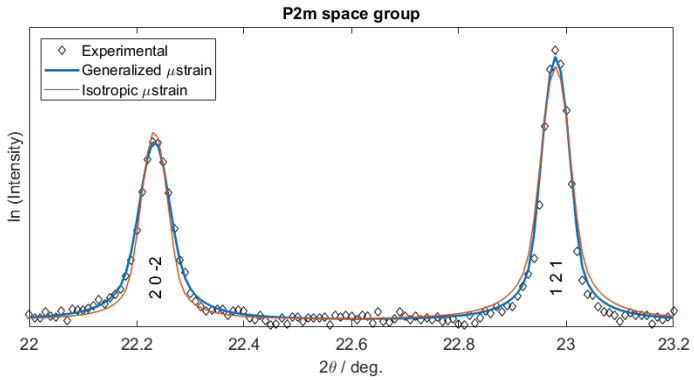

Figure S2. Detail of the Pawley refinement on the hydrated structure with *P2/m* space group.

Figure S3 reports the best fit of the Pawley refinement conducted by using a generalized μstrain model, which better describes the peak shape of different reflections (see below).

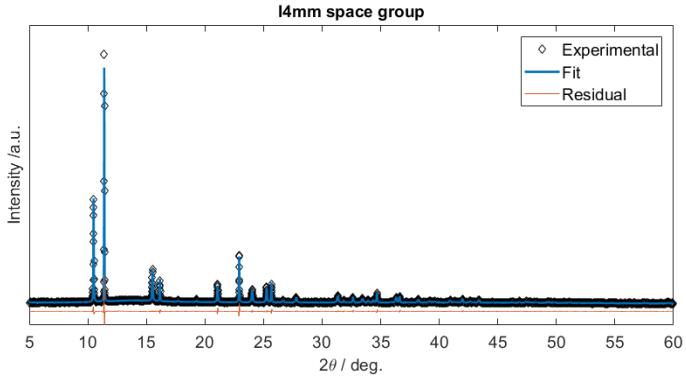

Figure S3. Pawley refinement on the anhydrous structure with *I4mm* space group and a generalized μstrain model.

The same considerations apply for the pattern of the anhydrous structure as well. **Figure S4** highlights the difference in refining the *(112)* and *(200)* reflections, being the generalized microstrain model more suitable to describe the peak shape at different angles. Moreover, **Figure S5** shows that the isotropic microstrain model fails in fitting the broader *(002)* and the narrower *(110)* reflections. As result of the adoption of the generalized μstrain model, the fit goodness improves significantly, the R_{wp} factor decreasing from 8.389% to 5.922%.

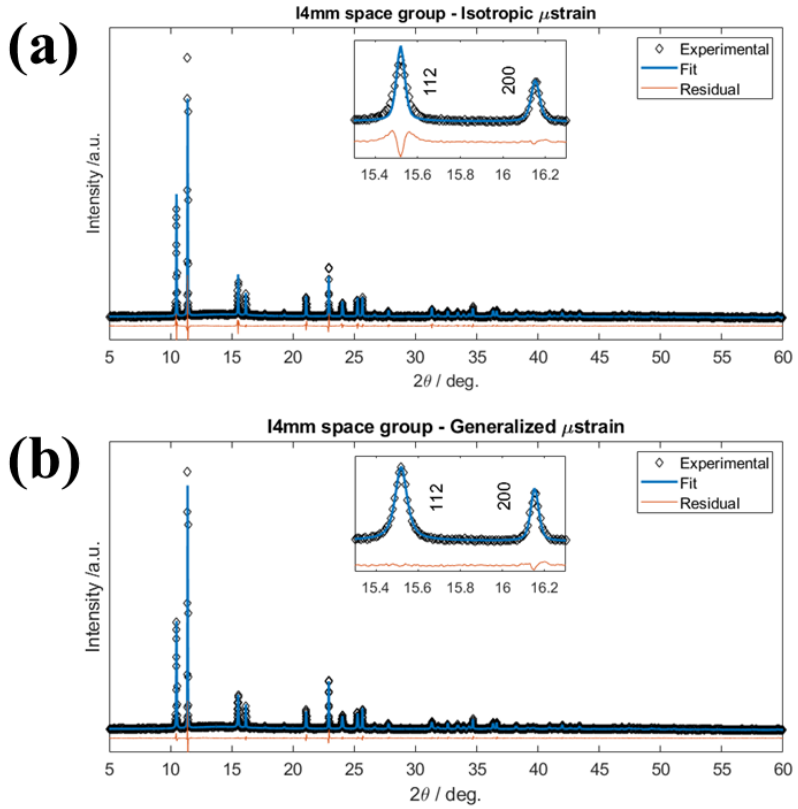

Figure S4. Pawley refinement on the anhydrous structure with *I4mm* space group. Panel **(a)** diplays the fit conducted by considering an isotropic μstrain model, while a generalized μstrain model was adopted in the refinement shown in panel **(b)**.

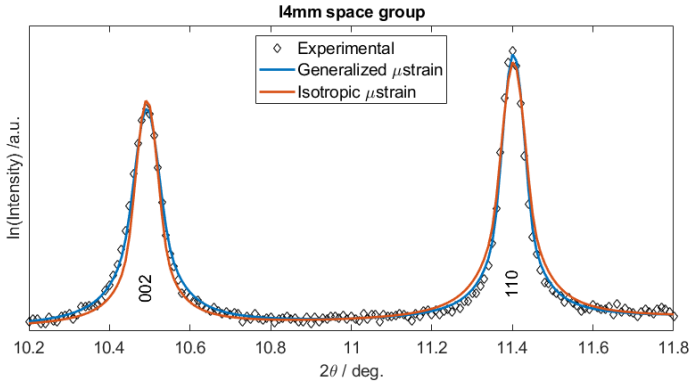

Figure S5. Detail of the Pawley refinement on the anhydrous structure with *I4mm* space group.

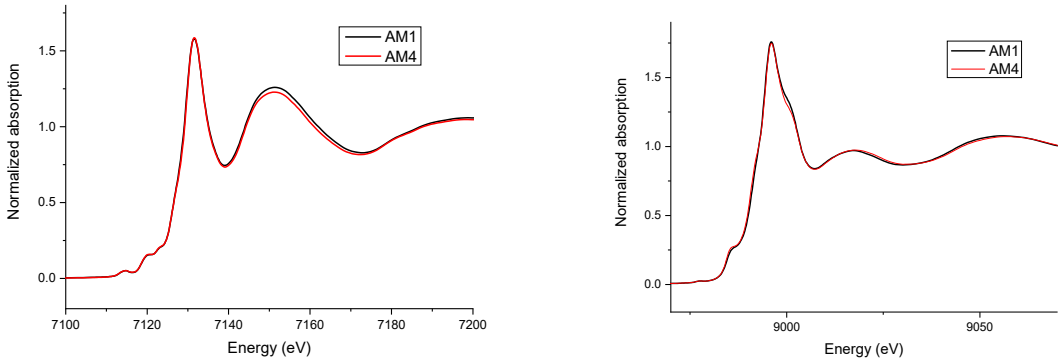

Figure S6. Comparison of the anhydrous and the hydrated structures of copper nitroprusside powders. The Fe K-edge is reported on the left, while the Cu K-edge is on the right. It is seen that the Cu and Fe local structure is closely the same. AM1 stands for dehydrated, AM4 for hydrated.

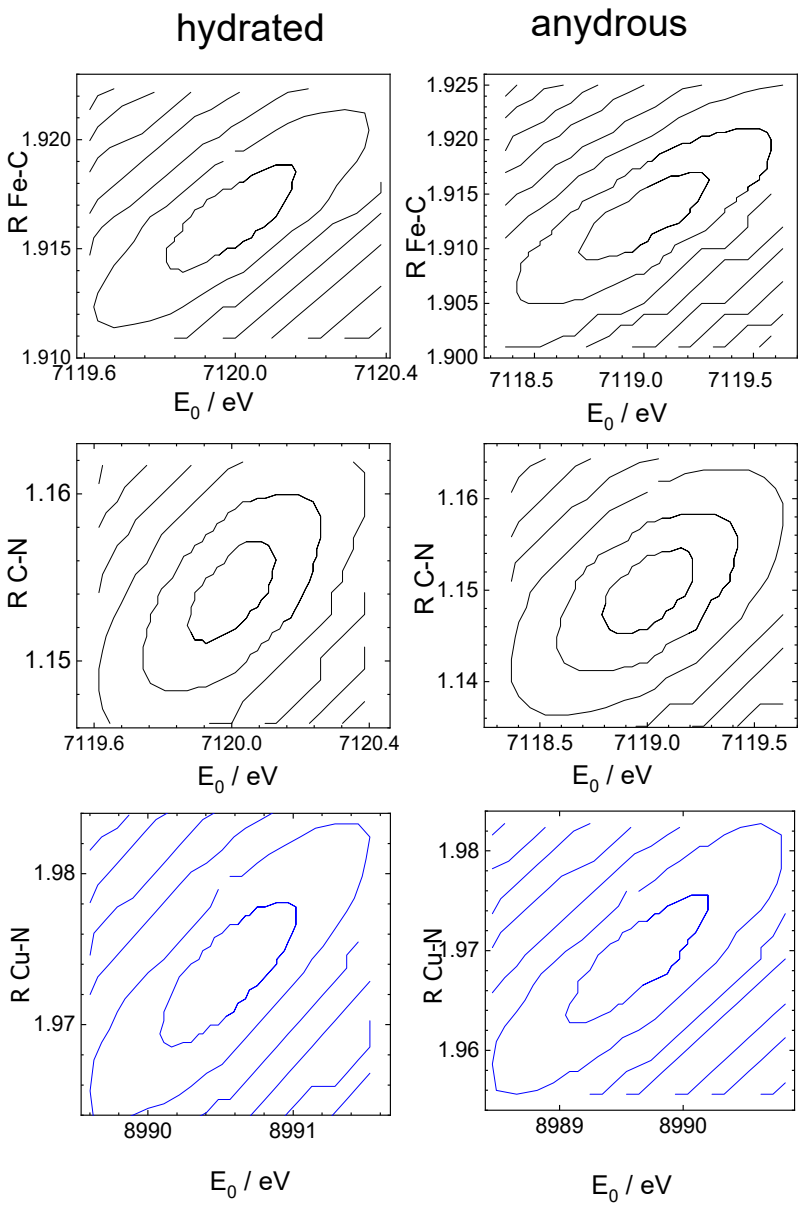

Figure S7. Examples of the two dimensional section of the parameter space (contour plots) for anhydrous and hydrated copper nitroprusside. These plots were selected among the parameters having strong correlation to reflect the highest error. The inner elliptical contour corresponds to

the 95% confidence level. Plots at the bottom are particular importance as they are referring to the Cu-N bond length quotation.

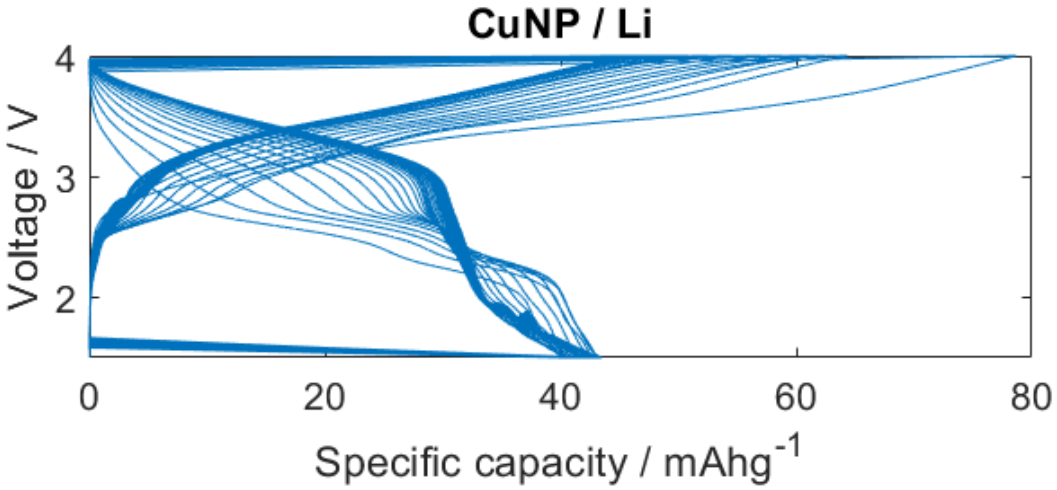

Figure S8. Voltage profile of CuNP against Li. Along cycling, the plateau at 2.2 V disappears, while the plateau at 2.8 V raises to 3.5 V.

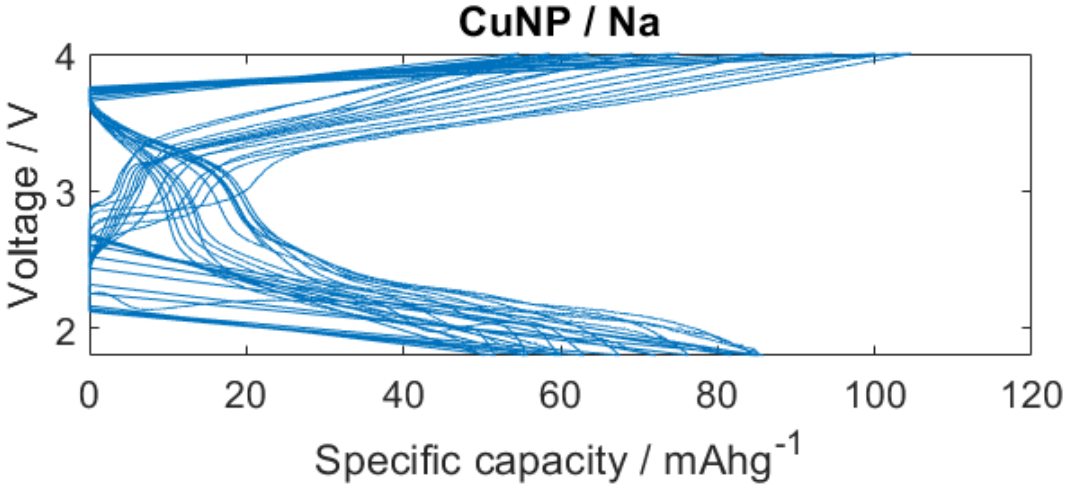

Figure S9. Voltage profile of CuNP against Na. Unlike Li, a slight activation causes an initial increase in specific capacity. Then, the capacity drops to about 20 mAh g^{-1}.

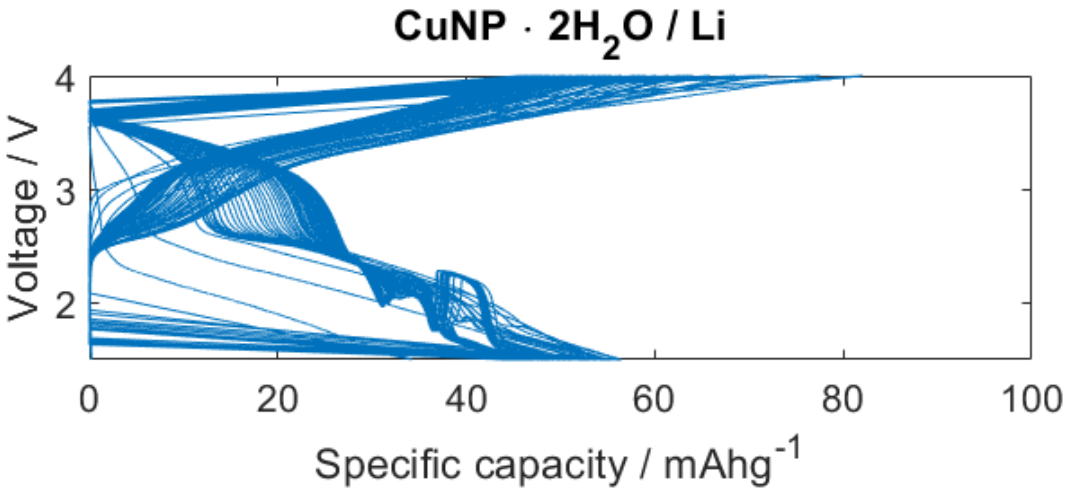

Figure S10. Voltage profile of CuNP $2H_2O$ against Li. The fade in capacity and change in voltage profile are similar to the anhydrous form of CuNP.

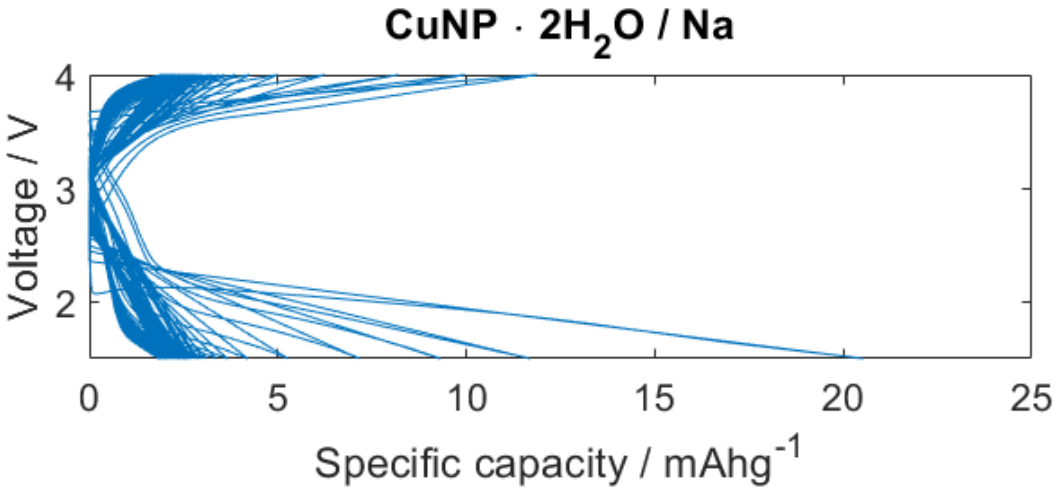

Figure S11. Voltage profile of CuNP $2H_2O$ against Na. The specific capacity decays rapidly and the material is not able to exchange Na-ions effectively.

Table S1. Results of the Rietveld refinement on the hydrated structure.

Space group	P 2/m							
Z	1							
Lattice parameters	a / Å = 6.4544(4)							
	b / Å = 7.44446(6)							
	c / Å = 6.4741(4)							
	α = γ = 90°							
	β = 111.9908(10)							
	V / Å^3 = 288.445(4)							
Microstrain "generalized" model (10^6 * ΔQ/Q) parameters								
S400 = 2811.677; S040 = 40.234; S004 = 1798.333 S220 = S202 = S022 = S301 = S103 = S121 = 0 (fixed) Gaussian/Lorentzian mix = 1.0 (fixed)								
wR factor	0.06397							
Atomic parameters								
Atom label	Atom Type	x coordinate	y coordinate	z coordinate	Occupancy	U isotropic	Site multiplicity	Site symmetry
Fe1	Fe	0.5 (fixed)	0.5 (fixed)	0.5 (fixed)	1.0 (fixed)	0.0245(7)	1	2/m
Cu1	Cu	0.0 (fixed)	0.0 (fixed)	0.0 (fixed)	1.0 (fixed)	0.0245 (=Fe1)	1	2/m
C1	C	0.7191(15)	0.3045(10)	0.6547(16)	1.0 (fixed)	0.010 (fixed)	4	1
C2	C	0.689(13)	0.5 (fixed)	0.328(13)	0.5 (fixed)	0.010 (fixed)	2	m
N1	N	0.1796(14)	0.1886(8)	0.2206(13)	1.0 (fixed)	0.010 (fixed)	4	1
N2	N	0.821(7)	0.5 (fixed)	0.219(5)	0.5 (fixed)	0.010 (fixed)	2	m
N3	N	0.661(12)	0.5 (fixed)	0.346(12)	0.5 (fixed)	0.058(11)	2	m
O1	O	0.7685(16)	0.0 (fixed)	0.2537(16)	1.0 (fixed)	0.020(4)	2	m
O2	O	0.259(9)	0.5 (fixed)	0.780(8)	0.5 (fixed)	0.190(25)	2	m

Relevant bond lengths		
Atom 1	Atom 2	Value / Å
Fe1	C1	2.015(7)
Fe1	N3	1.687(9)
Fe1	C2	1.933(9)
Cu1	N1	2.029(6)
Cu1	O1	2.414(9)
N3	O2	1.195(13)
C1	N1	1.195(6)
C2	N2	1.298(28)

Relevant bond angles			
Atom 1	Atom 2	Atom 3	Value / deg
Fe1	N3	O2	172(7)

Table S2. Results of the Rietveld refinement on the anhydrous structure.

Space group	I 4 m m
Z	2
Lattice parameters	a = b / Å = 7.35394(6)
	c / Å = 11.29887(13)
	α = β = γ = 90°
	V / Å^3 = 611.047(12)
Microstrain "generalized" model (10^6 * ΔQ/Q) parameters	
S400 = 1282.163; S004 = 1073.746; S022 = 5991.698 S220 = 0.000 (fixed) Gaussian/Lorentzian mix = 1.0 (fixed)	
wR factor	0.06099

Atomic parameters

Atom label	Atom Type	x coordinate	y coordinate	z coordinate	Occupancy	U isotropic	Site multiplicity	Site symmetry
Fe1	Fe	0.5 (fixed)	0.5 (fixed)	0.5445(5)	1.0 (fixed)	0.0250(8)	2	4mm
Cu1	Cu	0.5 (fixed)	0.5 (fixed)	0.0658(6)	1.0 (fixed)	0.0250 (=Fe1)	2	4mm
C1	C	0.6873(9)	0.3127 (fixed)	0.5382(17)	1.0 (fixed)	0.0186(23)	8	m
C2	C	0.5 (fixed)	0.5 (fixed)	0.3721(8)	1.0 (fixed)	0.086(11)	2	4mm
N1	N	0.0 (fixed)	0.0 (fixed)	0.7538(15)	1.0 (fixed)	0.086 (=C2)	2	4mm
N2	N	0.3028(8)	0.3028 (fixed)	0.0389(13)	1.0 (fixed)	0.0186(23) (=C1)	8	m
N3	N	0.0 (fixed)	0.0 (fixed)	0.1863(15)	1.0 (fixed)	0.065(14)	2	4mm
O1	O	0.5 (fixed)	0.5 (fixed)	0.7863(16)	1.0 (fixed)	0.056(9)	2	4mm
O2	O	0.5 (fixed)	0.0 (fixed)	0.435(25)	0.042	0.18(15)	4	mm2

Relevant bond lengths

Atom 1	Atom 2	Value / Å
Fe1	C1	1.950(5)
Fe1	N3	1.602(22)
Fe1	C2	1.948(8)
Cu1	N1	2.124(16)
Cu1	N2	2.074(4)
N3	O1	1.129(8)
C2	N1	1.336(18)
C1	N2	1.200(3)

Relevant bond angles

Atom 1	Atom 2	Atom 3	Value / deg
Fe1	N3	O1	180 (fixed)