Electronic Supplementary Material (ESI) for Dalton Transactions.

SUPPORTING INFO

Protein-mediated disproportionation of Au(I): insights from the structures of adducts of Au(III) compounds bearing N,N-pyridylbenzimidazole derivatives with lysozyme

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Table S1. Data collection and refinement statistics

Data collection	HEWL-**1**	HEWL-**1**	HEWL-**1**	HEWL-**2**	HEWL-**2**
Soaking time	21 h	24 h	3 days	21 h	24 h
Space group	$P4_32_12$	$P4_32_12$	$P4_32_12$	$P4_32_12$	$P4_32_12$
Wavelength (Å)	1.5418	1.5418	1.5418	1.5418	1.5418
Unit cell parameter					
a (Å)	76.953	78.328	77.448	76.735	77.844
b (Å)	76.953	78.328	77.448	76.735	77.844
c (Å)	38.889	37.691	37.316	38.981	37.459
α(°)	90.0	90.0	90.0	90.0	90.0
β(°)	90.0	90.0	90.0	90.0	90.0
γ(°)	90.0	90.0	90.0	90.0	90.0
Observed reflections	54007	36915	68574	78741	29959
Unique reflections	8955	6962	8972	11577	6011
Resolution (Å)	34.73-1.95 (1.98-1.95)	55.39-2.12 (2.16-2.12)	30.86-1.90 (1.93-1.90)	34.78-1.78 (1.81-1.78)	33.78-2.22 (2.26-2.22)
Completeness (%)	99.8 (99.8)	98.3 (97.2)	95.0 (89.3)	99.1 (95.0)	98.8 (99.3)
Anomalous completeness (%)	99.5 (97.2)	98.0 (90.5)	94.7 (84.7)	99.0 (92.5)	98.6 (94.7)
R_{merge} (%)	14.1 (54.6)	13.2 (64.5)	10.7 (65.2)	12.1 (48.3)	13.3 (63.9)
R_{pim} (%)	6.0 (36.1)	6.0 (35.8)	4.4 (36.0)	4.6 (27.8)	6.4 (37.0)
$CC_{1/2}$	0.805	0.752	0.648	0.830	0.722
Cc* last shell	0.951	0.927	0.887	0.952	0.916
I/σ(I)	13.8 (1.5)	10.4 (1.6)	22.8 (1.3)	19.4 (1.8)	10.1 (1.3)
Multiplicity	6.0 (3.1)	5.3 (3.7)	7.7 (4.3)	6.8 (3.6)	5.0 (3.5)
Total data collection time (s)	600	375	630	600	350
<u>Refinement</u>					
Resolution (Å)	34.73-1.95	55.39-2.12	30.86-1.90	34.78-1.78	33.78-2.22
N. reflections	8452	6574	8489	10927	5659
N. reflections in test set	466	359	465	620	337
R_{factor} (%)	19.2	21.0	15.8	15.6	17.4
R_{free} (%)	26.0	29.4	21.5	22.3	24.9
Rall (%)	19.6	21.5	16.1	16.0	17.9
N. non-H atoms	1156	1186	1210	1332	1140
Mean B-value (Å)	22.6	24.7	28.2	20.2	33.4
<u>Ramachandran plot statistics</u>					
Most favoured (%)	95.8	90.1	95.6	95.9	96.8
Additional allowed	4.2	7.9	3.4	4.1	3.2
Generously allowed/ Disallowed (number of residues)	0	2	0	0	0
R.m.s.d. bonds (Å)	0.008	0.007	0.008	0.009	0.009
R.m.s.d. angles (°)	1.52	1.56	1.51	1.56	1.69

Values in parenthesis refer to last resolution shell

Table S2. Intensities of peaks observed in the Fo-Fc electron density map calculated using PDB code 193L as model, just after the molecular and in the anomalous difference electron density map.

	HEWL-**1**	HEWL-**1**	HEWL-**1**	HEWL-**2**	HEWL-**2**
	21 h	24 h	3 days	21 h	24 h
λ used for data collection	0.15418 nm	0.15418 nm	0.15418 nm	0.15418 nm	0.15418 nm
Resolution (Å)	34.73-1.95	55.39-2.12	30.86-1.90	34.78-1.78	33.78-2.22
Peaks in the Fo-Fc electron density map calculated using PDB code 193L as model, just after the molecular replacement	The three gold binding sites correspond to the first, the second and the 11th peak in the Fo-Fc electron density map. Peak 1: 13.65 sigma=assigned to Au2 Peak 2: 9.15 sigma=assigned to Au3 Peak3:6.47 sigma=assigned to nitrate406 Peak4:6.40 sigma=assigned to HOH2 Peak5:6.39 sigma=assigned to HOH1 Peak6:6.21 sigma=assigned to HOH3 Peak7:6.00 sigma=assigned to EDO302 Peak8:5.94 sigma=assigned	The gold binding site corresponds to the first peak in the Fo-Fc electron density map. Peak 1: 16.65 sigma=assigned to Au1 The map has been calculated with an unbiased model that refines to Rfactor=31.3, Rfree=32.9	The three gold binding sites correspond to the first, the second and the fourth peak in the Fo-Fc electron density map. Peak 1: 15.25 sigma=assigned to Au2 Peak 2: 11.07 sigma=assigned to Au1 Peak 3: 8.79 sigma=assigned to HOH1 Peak 4: 7.59 sigma=assigned to Au3 The map has been calculated with an unbiased model that refines to Rfactor=31.3, Rfree=32.9	The three gold binding sites correspond to the first, the second and third peak in the Fo-Fc electron density map. Peak 1: 19.83 sigma=assigned to Au2 Peak 2: 15.16 sigma=assigned to Au1 Peak 3: 14.08 sigma=assigned to Au3 The map has been calculated with an unbiased model that refines to Rfactor=33.7, Rfree=34.8	The three gold binding sites correspond to the first, the second and fourth peak in the Fo-Fc electron density map. Peak 1: 11.42 sigma=assigned to Au1 Peak 2: 8.76 sigma=assigned to Au2 Peak3:7.59 sigma=assigned to EDO201302 Peak 4: 7.03 sigma=assigned to Au32

	to alternative conformation of side chain of Asp18 Peak9:5.71 sigma=assigned to nitrate407 Peak10:5.50 sigma=assigned to HOH40 Peak 11: 5.50 sigma=assigned to Au1 The map has been calculated with an unbiased model that refines to Rfactor=32.3, Rfree=32.1				
Peaks in the anomalous difference electron density map calculated using refined PDB structures (without gold atoms) as model.	Au2 corresponds to the first peak in the anomalous difference electron density map (10.91 sigma); Au3 corresponds to a peak in the anomalous map at 3.2 sigma; Au1 has low anomalous signal, but this could be due to the very low occupancy of this gold binding site	Au1 corresponds to the first peak in the anomalous difference electron density map (10.91 sigma).	Au2 corresponds to the first peak in the anomalous difference electron density map (13.3 sigma); Au1 corresponds to the second peak in the anomalous difference electron density map at 11.7 sigma; Au3 corresponds to the third peak in the anomalous difference	Au2 corresponds to the first peak in the anomalous difference electron density map (18.0 sigma); Au1 corresponds to the second peak in the anomalous difference electron density map (16.8 sigma); Au3 corresponds to the third peak in the anomalous difference	Au1 corresponds to the first peak in the anomalous difference electron density map (5.1 sigma); Au2 corresponds to the second peak in the anomalous difference electron density map (5.1 sigma); Au3 corresponds to a peak in the

			electron density map at 7.04 sigma	electron density map (14.7 sigma);	anomalous map at 2.9sigma;

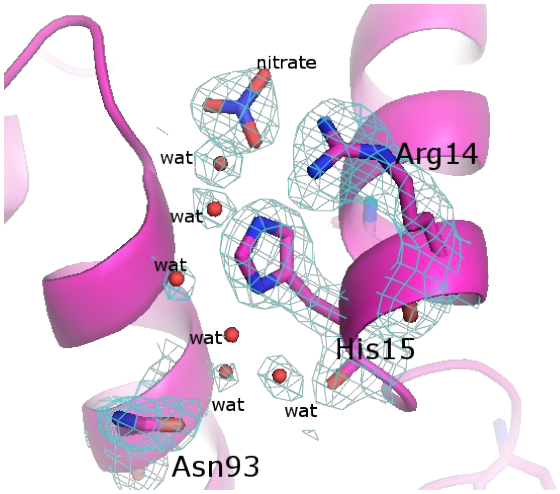


Figure S1. 2Fo-Fc electron density map close to the side chains of His15 and Asn93 in the structure of the adduct formed in the reaction between HEWL and **1** after 3 days of soaking. Gold atoms are not found in this structure, suggesting that the adduct has lost metal centres with time.

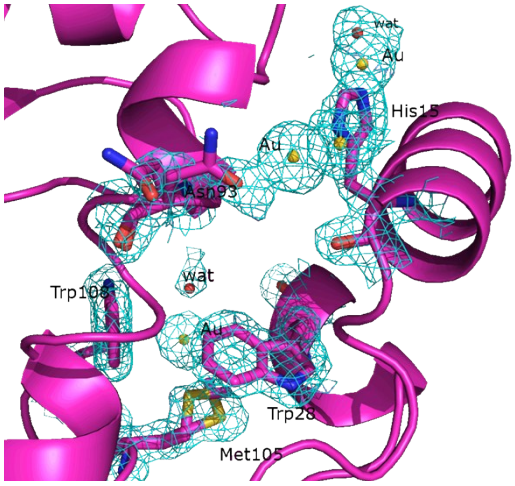


Figure S2. 2Fo-Fc electron density map (1.0 σ, cyan) of the Au binding site in the structure of the adduct formed in the reaction between HEWL and **2** after 21 h of soaking.

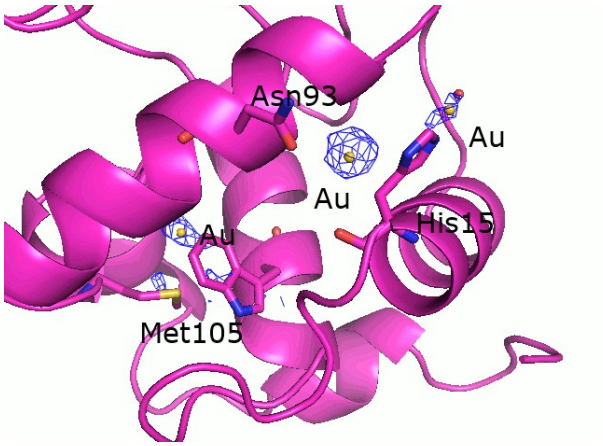
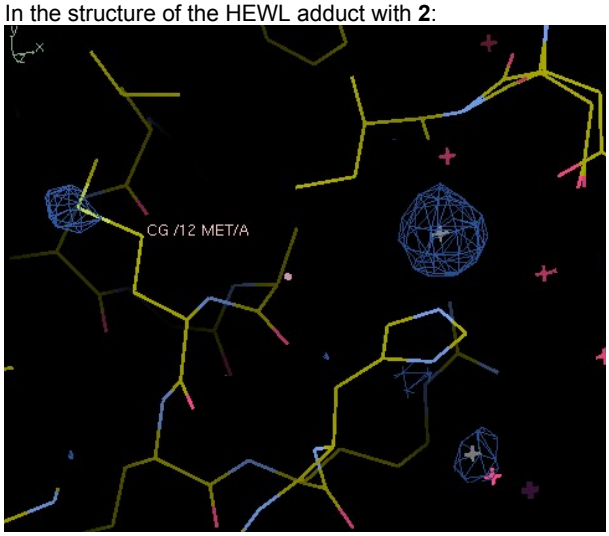


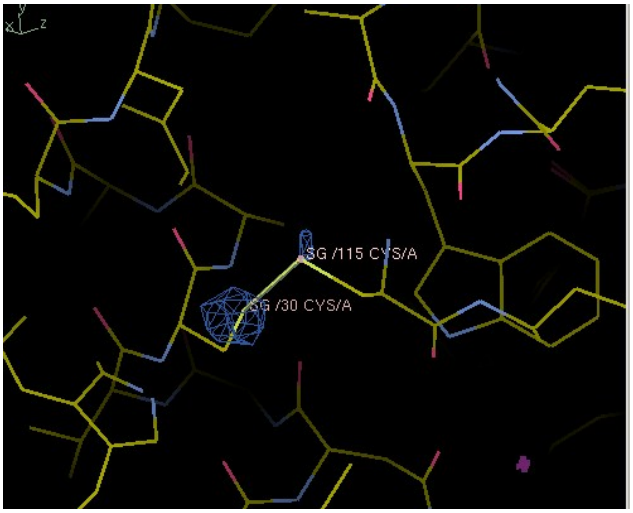
Figure S3. Anomalous difference electron density map (2.5 σ, cyan) of the Au binding sites in the structure of the adduct formed in the reaction between HEWL and **2** after 1 day of soaking.

S atoms of protein residues can be observed only in high quality anomalous difference electron density maps for data collected using CuKα (f''=0.56e$^-$). In this respect, it is interesting to note that in our structures of HEWL adducts with **1** (24 h incubation) and **2** (21 h incubation), signals of Cys and Met can be clearly observed in the anomalous difference electron density maps.
See below:

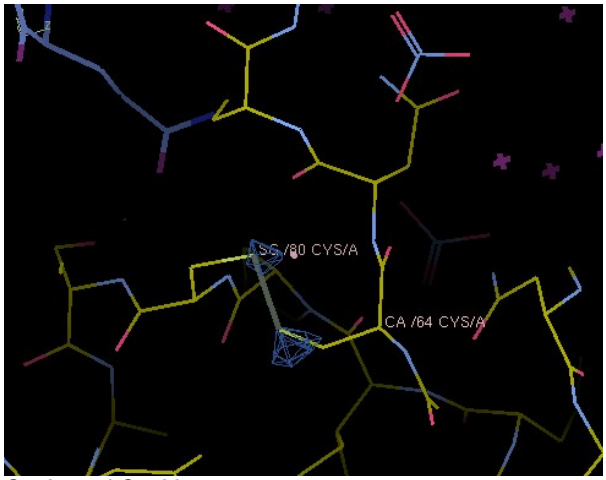
In the structure of the HEWL adduct with **2**:



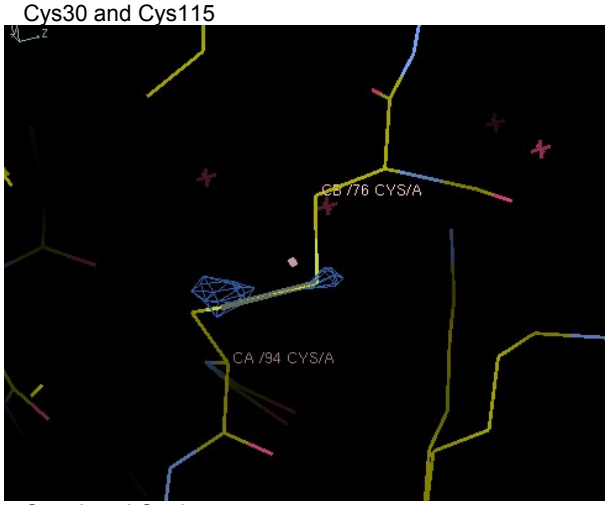
Met12 and Au



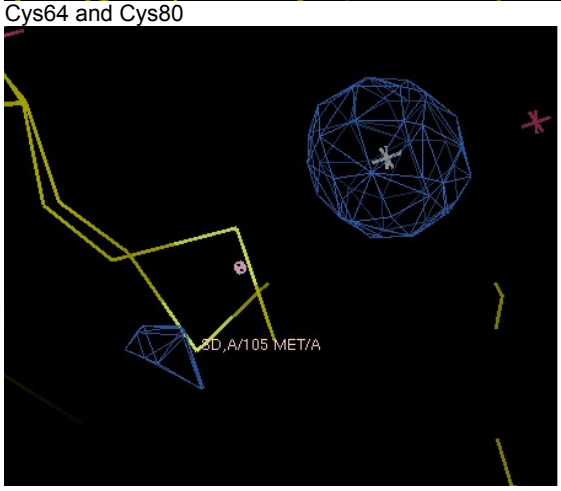
Cys30 and Cys115



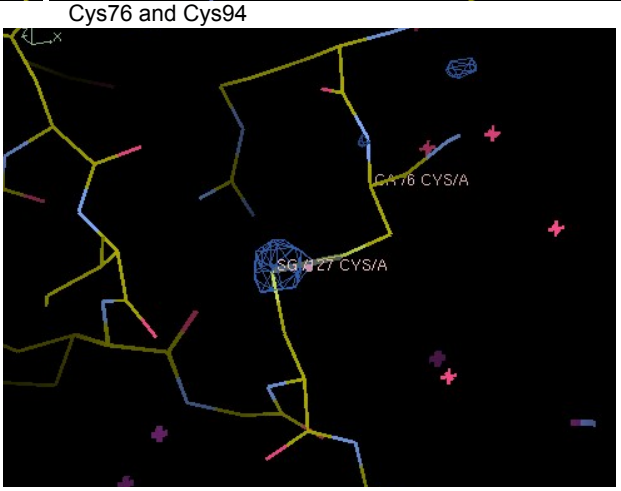
Cys64 and Cys80



Cys76 and Cys94

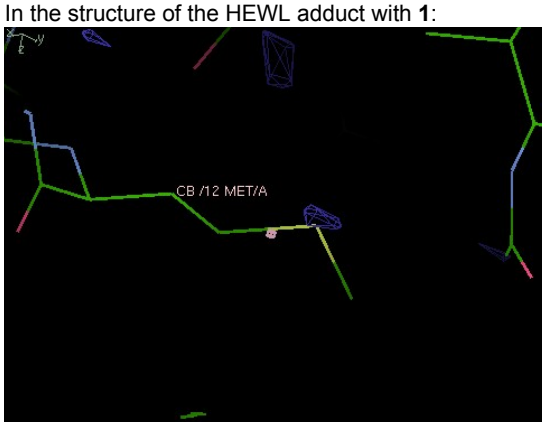


Met105 and Au

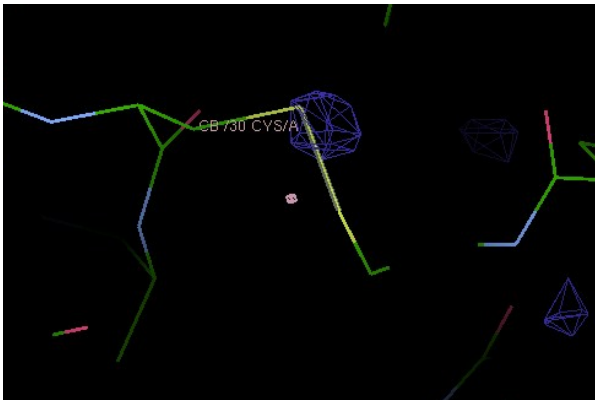


Cys127

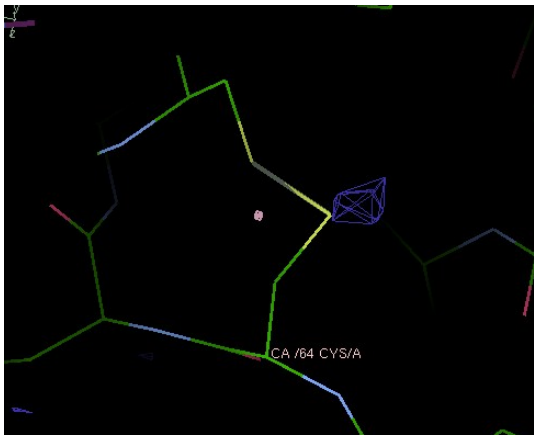
In the structure of the HEWL adduct with **1**:



Met12



Cys30



Cys64

Cys94