Supporting Information

Is transition metal phthalocyanines active for urea synthesis via electrocatalytic coupling of CO_2 and N_2?

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Contents

This supplementary information contains the details for the calculation of free energy correction, the optimized structure of CON_2 (Figure S1), projected density of states of CO and N2 on FePc(Figure S2), energy-decomposition analysis(Figure S3), and all the intermediates for CO-N2 coupling to urea on Ti, V, Zr and HfPc (Figure S4), and free energy sufaces for CO2 reduction to CO (Figure S5).

Free energy corrections

The free energy corrections include

$$\Delta G_{corr} = \Delta G_{ZPE} + \int C_p dT - TS$$

in which ZPE stands for zero-point energy, $\int C_p dT$ is the enthalpic thermal corrections, and -TS is the entropy correction. With the vibration frequency calculated with VASP, these three terms were calculated with Atomic Simulation Envionment package.
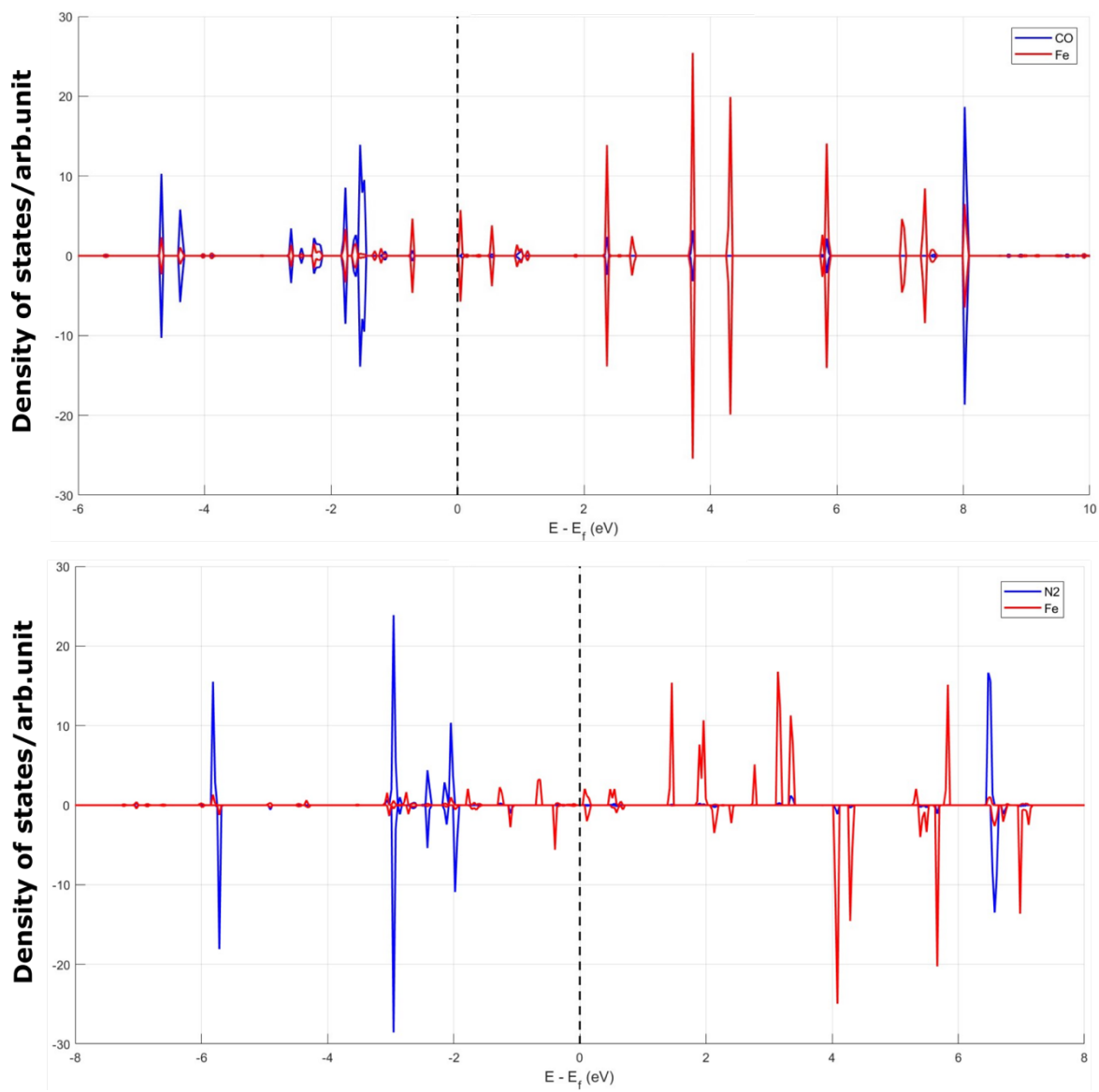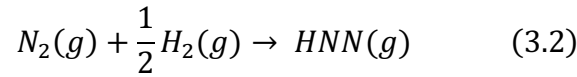
Figure S1. The projected density of states of CO and N2 on FePc. E_f is the Fermi energy.
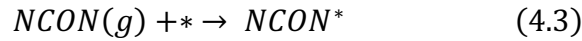
Energy-decomposition analysis

$$N_2^* + H^+ + e^- \rightarrow HNN^* \qquad\qquad (3)$$

$$N_2^* + CO(g) \rightarrow NCON^* \qquad\qquad (4)$$

We decompose ΔG_3 at 0.0 V$_{\text{RHE}}$ into the reaction free energy of the following reactions:

$$N_2^* \rightarrow * + N_2(g) \qquad\qquad (3.1)$$

$$N_2(g) + \frac{1}{2} H_2(g) \rightarrow HNN(g) \qquad\qquad (3.2)$$

$$HNN(g) + * \rightarrow HNN^* \qquad\qquad (3.3)$$

Note that the energy of $(H^+ + e^-)$ is related to that of H$_2$(g) in reaction (3.2). Similarly, ΔG_4 can be decomposed into reaction free energy of reaction 3.1 and 4.2, 4.3

$$N_2(g) + CO(g) \rightarrow NCON(g) \qquad\qquad (4.2)$$

$$NCON(g) + * \rightarrow NCON^* \qquad\qquad (4.3)$$
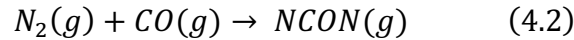
Then:

$$\Delta G_4 - \Delta G_3 = (\Delta G_{4.2} - \Delta G_{3.2}) + (\Delta G_{4.3} - \Delta G_{3.3}) = \Delta G_g + \Delta G_{ads}$$

In which $\Delta G_g = G_{4.2} - \Delta G_{3.2} = 1.17\ eV$ is constant for all the MPcs. ΔG_{ads} is the difference in the adsorption free energy of NCON and HNN (ΔG_{ads}(NCON)- ΔG_{ads}(HNN)). ΔG_g is very high probably because the formation of NCON(g) needs to break all the triple bonds in N$_2$, while the formation of HNN only needs to break one of the triple bonds. Therefore, only when ΔG_{ads} is lower than -1.17 eV, CO-N$_2$ coupling becomes more favorable than N$_2$ reduction. As shown in Figure S3, although $\Delta G_{4.3}$, i.e. ΔG_{ads} (NCON) is always lower than $\Delta G_{4.3}$ i.e. ΔG_{ads}(HNN), the difference in only lower than -1.17 eV in the scenarios of strong adsorption. This is because ΔG_{ads} (NCON) scale with ΔG_{ads} (HNN) and the slop is larger than one, therefore, ΔG_{ads} also increases with ΔG_{ads}(HNN). ΔG_{ads} then becomes negative than -1.17

eV when ΔG_{ads}(HNN) is low enough. Therefore, the reason that TiPc, VPc, ZrPc, and HfPc prefers NCON is that the formation of NCON requires too much energy input which only can be compensated when the adsorption of NCON is strong enough. The key here is the slop for the ΔG_{ads}(NCON) scaling line is larger than 1, and the reason is that NCON has more dangling bonds (J. K. Nørskov, et al., Physical Reviews Letters 99, 016105, 2007).
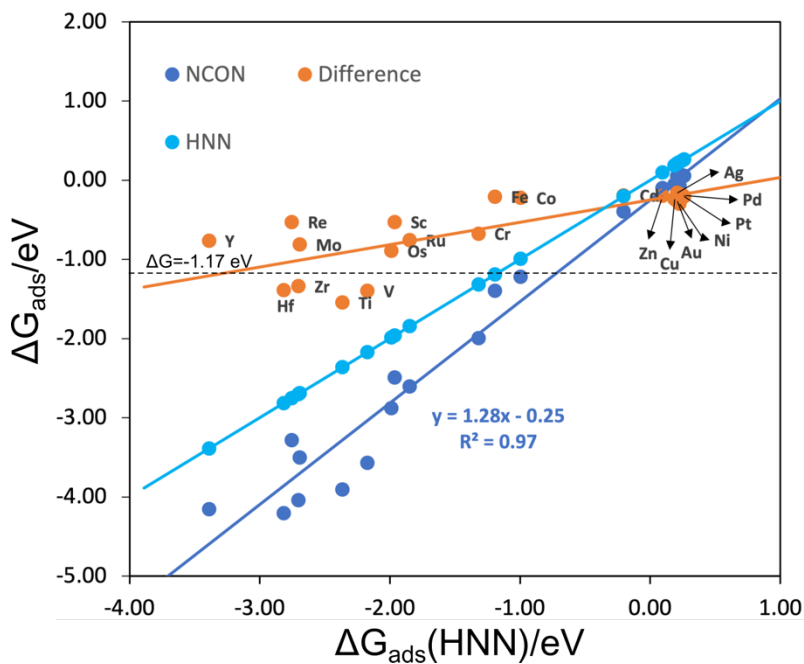

Figure S2 the adsorption free energies of NCON and HNN, and their difference. The dashed horizontal line is where the difference is equal to -1.17 eV.
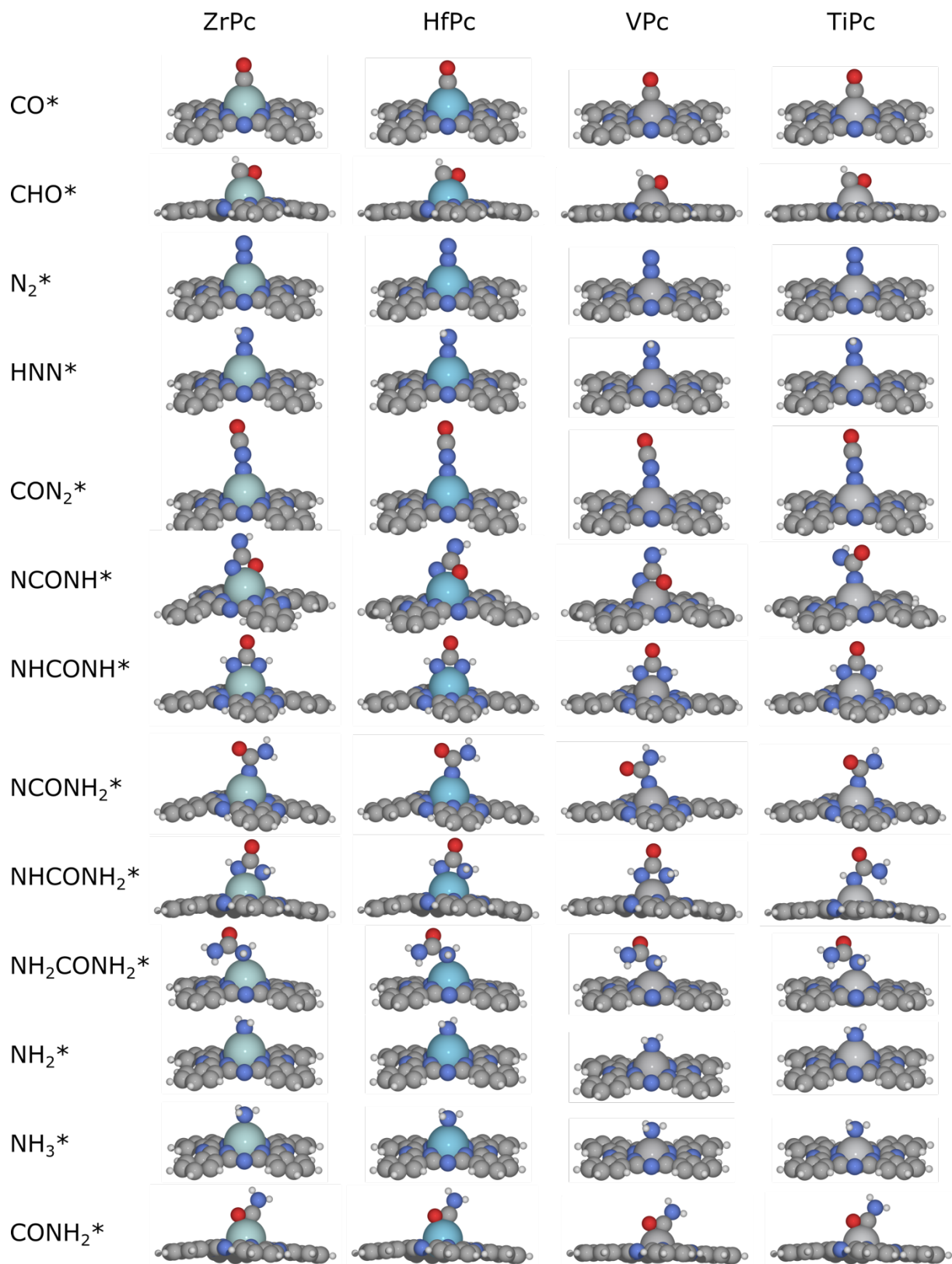
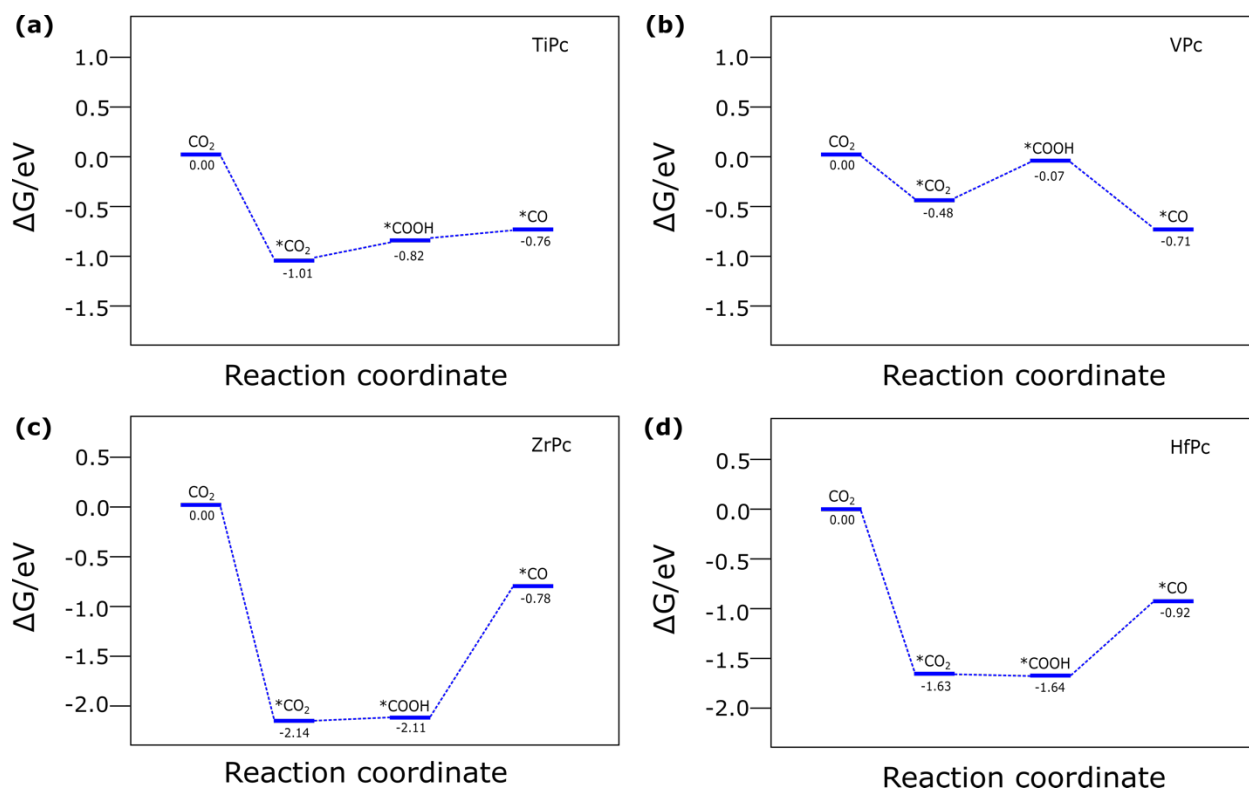Figure S3, the optimized structures of the intermediates on Ti, V, Zr, and HfPc.

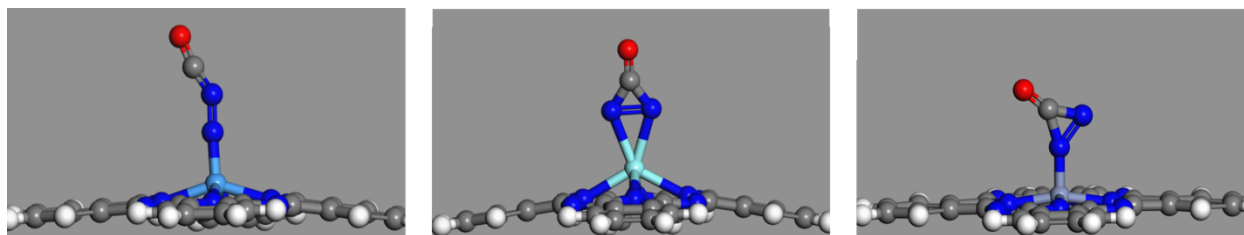Figure S4. Free energy surfaces for CO_2 reduction to CO* on TiPc, VPc, ZrPc, and HfPc.

Figure S5, three adsorption structures of CON_2 on MPc, from left to right: linear, η_2 and η_1.

Table S1 The data for Figure 2-3 (G_{ads}(N_2 in Table S2)

Metal	G(CO2*)	Gads(CO*)	G(CO*)	G(CHO*)	G(*NCON)	Delta_G 1	Delta_G 2	Dlelta_G 3	Delta_G 4
Ag	0.02	0.61	0.82	2.04	3.82	1.22	3.01	2.38	3.22
Au	0.03	0.61	0.82	2.10	3.72	1.28	2.90	2.38	3.11
Cd	-0.18	0.45	0.66	1.47	3.38	0.82	2.72	2.17	2.97
Co	-0.04	-0.19	0.02	-0.17	2.55	-0.19	2.54	1.40	2.17
Cr	0.00	-0.03	0.18	0.54	1.78	0.36	1.60	0.88	1.20
Cu	0.02	0.56	0.77	1.90	3.72	1.13	2.95	2.36	3.12
Fe	-0.02	-0.91	-0.70	0.15	2.40	0.85	3.10	1.35	2.17
Hf	-2.18	-1.67	-1.46	-1.75	-0.98	-0.29	0.48	1.14	0.20
Ir	-0.01	-0.37	-0.16	-0.87	2.82	-0.71	2.98	0.75	2.15
Mn	-0.03	-0.52	-0.31	0.38	2.22	0.70	2.54	1.20	1.69
Mo	-0.51	-1.13	-0.92	-0.43	0.27	0.49	1.19	0.31	0.49
Nb	-1.46	-1.41	-1.20	-1.12	-0.55	0.07	0.65	0.38	0.05
Ni	0.00	0.56	0.77	1.64	3.70	0.87	2.93	2.40	3.09
Os	-0.25	-2.26	-2.05	-0.82	0.89	1.23	2.94	1.37	1.47
Pd	0.00	0.58	0.79	2.01	3.83	1.22	3.04	2.42	3.22
Pt	-0.01	0.58	0.79	1.97	3.83	1.18	3.04	2.43	3.22
Re	-0.51	-2.09	-1.88	-0.44	0.49	1.44	2.37	0.62	1.08
Rh	-0.02	-0.28	-0.07	-0.74	2.85	-0.66	2.92	0.95	2.35
Ru	-0.07	-2.02	-1.81	-0.59	1.17	1.22	2.98	1.50	1.74
Sc	-0.55	-0.29	-0.08	-0.30	1.28	-0.22	1.36	0.88	1.34
Ta	-1.52	-1.51	-1.30	-1.43	-0.68	-0.13	0.62	0.29	-0.03
Ti	-1.01	-0.97	-0.76	-0.61	-0.14	0.15	0.63	0.91	0.36
V	-0.48	-0.92	-0.71	-0.22	0.18	0.49	0.90	1.01	0.59
W	-0.89	-1.66	-1.45	-0.94	-0.25	0.51	1.20	0.19	0.16
Y	-2.12	-1.73	-1.52	-1.77	-0.38	-0.25	1.14	0.92	1.15
Zn	0.04	0.52	0.73	1.88	3.67	1.14	2.94	2.29	3.09
Zr	-1.48	-0.99	-0.78	-1.05	-0.27	-0.27	0.50	0.59	0.24

Tabel S2 data for Figure 6

Metal	Gads(N2)	G(HNN)	G(NH2)	G(NH3)	G(HNN)-G(N2)	G(NH3)-G(NH2)	Gads(NH2)	Gads(CONH2)
Ag	0.39	2.78	1.66	-0.48	2.34	-2.13	0.34	0.20
Au	0.40	2.78	1.59	-0.48	2.33	-2.07	0.27	0.25
Cd	0.20	2.36	0.64	-1.29	2.12	-1.93	-0.68	-0.40
Co	0.17	1.57	0.17	-1.06	1.35	-1.23	-1.15	-1.75
Cr	0.37	1.25	-0.30	-0.76	0.84	-0.46	-1.62	-1.25
Cu	0.39	2.75	1.51	-0.54	2.32	-2.06	0.20	0.09
Fe	0.02	1.38	-0.09	-0.95	1.33	-0.86	-1.41	-1.48
Hf	-1.39	-0.25	-2.95	-1.97	0.55	0.98	-4.27	-3.47
Ir	0.46	1.20	-0.38	-0.88	0.70	-0.51	-1.69	-2.47
Mn	0.32	1.53	0.05	-0.94	1.16	-0.98	-1.27	-1.27
Mo	-0.44	-0.12	-1.57	-1.32	0.27	0.25	-2.89	-2.00
Nb	-0.81	-0.43	-2.42	-1.64	0.22	0.78	-3.73	-3.00
Ni	0.40	2.79	1.47	-0.39	2.35	-1.86	0.15	0.00
Os	-0.79	0.58	-1.10	-0.89	1.33	0.20	-2.41	-2.43
Pd	0.40	2.82	1.64	-0.35	2.37	-1.99	0.32	0.23
Pt	0.40	2.83	1.63	-0.31	2.38	-1.95	0.32	0.24
Re	-0.80	-0.19	-1.67	-0.93	0.57	0.73	-2.98	-2.39
Rh	0.29	1.24	-0.30	-1.03	0.89	-0.73	-1.62	-2.34
Ru	-0.78	0.72	-0.88	-1.67	1.46	-0.79	-2.20	-2.23
Sc	-0.27	0.60	-1.84	-1.74	0.83	0.10	-3.16	-2.50
Ta	-0.86	-0.57	-2.50	-1.67	0.25	0.83	-3.82	-3.31
Ti	-0.71	0.20	-2.09	-1.87	0.87	0.22	-3.41	-2.66
V	-0.61	0.40	-1.72	-1.77	0.95	-0.05	-3.04	-2.19
W	-0.62	-0.43	-2.20	-1.36	0.15	0.84	-3.52	-2.30
Y	-1.74	-0.82	-3.27	-3.14	0.87	0.13	-4.59	-4.01
Zn	0.37	2.66	1.21	-0.91	2.25	-2.12	-0.10	0.00
Zr	-0.72	-0.13	-2.69	-1.85	0.54	0.84	-4.01	-3.26