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

Pressure-induced non-innocence in bis(1,2-dionedioximato)Pt(II) complexes: an experimental and theoretical study of their insulator-metal transitions

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Crystallographic data for $Pt(bqd)_2$

Table S1: *Summary of the crystallographic information obtained for $Pt(bqd)_2$ at each pressure point.*

	Ambient	**0.11 GPa**	**0.16 GPa**	**0.29 GPa**	**0.58 GPa**	**1.03 GPa**	**1.47 GPa**	**1.98 GPa**	**2.38 GPa**
a / Å	9.7525(3)	9.7489(10)	9.7361(8)	9.7115(8)	9.6689(7)	9.6376(8)	9.6249(11)	9.5883(19)	9.5805(9)
b / Å	20.6661(6)	20.623(18)	20.626(13)	20.570(13)	20.509(11)	20.354(14)	20.271(19)	20.186(15)	20.129(16)
c / Å	6.3580(2)	6.3270(9)	6.3029(7)	6.2627(7)	6.1816(5)	6.0986(6)	5.9805(10)	5.8532(9)	5.8077(9)
α	90	90	90	90	90	90	90	90	90
β	90	90	90	90	90	90	90	90	90
γ	90	90	90	90	90	90	90	90	90
V / $Å^3$	1281.43(7)	1272.05(18)	1265.74(15)	1251.06(15)	1225.80(11)	1196.31(12)	1166.8(2)	1132.89(18)	1120.00(16)
Space Group	*Ibam*	*Ibam*	*Ibam*	*Ibam*	*Ibam*	*Ibam*	*Ibam*	*Ibam*	*Ibam*
λ / Å	0.71 (Mo Kα)	0.49	0.49	0.49	0.49	0.49	0.49	0.49	0.49
Completeness	99.9%	43.6%	46.8%	47.9%	47.1%	49.0%	47.2%	48.0%	47.7%
Resolution / Å	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80
R_{int}	0.051	0.071	0.066	0.059	0.047	0.074	0.065	0.056	0.057
R_1	0.022	0.035	0.035	0.027	0.020	0.033	0.069	0.075	0.083

Table S2: *Summary of specific bond lengths/angles and torsion angles within crystal packing of $Pt(bqd)_2$ throughout the pressure series.*

Pressure (GPa)	Pt-N bond lengths (Å)	N-Pt-N angles (°)	N-Pt…Pt-N torsion angles (°)
Ambient	1.986(10), 1.987(11)	79.7(6), 100.3(6)	87.4(4), 92.6(4)
0.11	2.000(19), 1.983(10)	80.1(7), 99.9(7)	87.7(5), 92.3(5)
0.16	1.96(2), 1.980(11)	81.0(8), 99.0(8)	88.0(6), 92.0(6)
0.29	1.981(19), 1.994(9)	80.7(7), 99.3(7)	87.9(5), 92.1(5)
0.58	1.957(14), 1.977(7)	80.5(6), 99.5(6)	88.2(4), 91.8(4)
1.03	2.04(2), 2.002(10)	78.5(7), 101.5(7)	87.4(5), 92.6(5)
1.47	1.99(3), 1.988(16)	79.8(10), 100.2(10)	88.9(9), 91.1(9)
1.98	2.01(4), 1.964(17)	79.8(11), 100.2(11)	88.2(9), 91.8(9)
2.38	2.00(4), 1.972(17)	79.3(12), 100.8(12)	88.9(10), 91.1(10)

Equation of state fitting

The pressure and cell volumes were fit using a 3rd order Birch-Murnaghan EoS:

$$P(V) = \frac{3B_0}{2}\left[\left(\frac{V_0}{V}\right)^{\frac{7}{3}} - \left(\frac{V_0}{V}\right)^{\frac{5}{3}}\right]\left\{1 + \frac{3}{4}\left(B_0^{'} - 4\right)\left[\left(\frac{V_0}{V}\right)^{\frac{2}{3}} - 1\right]\right\}$$

where B_0 = the bulk modulus and B_0' = its derivative

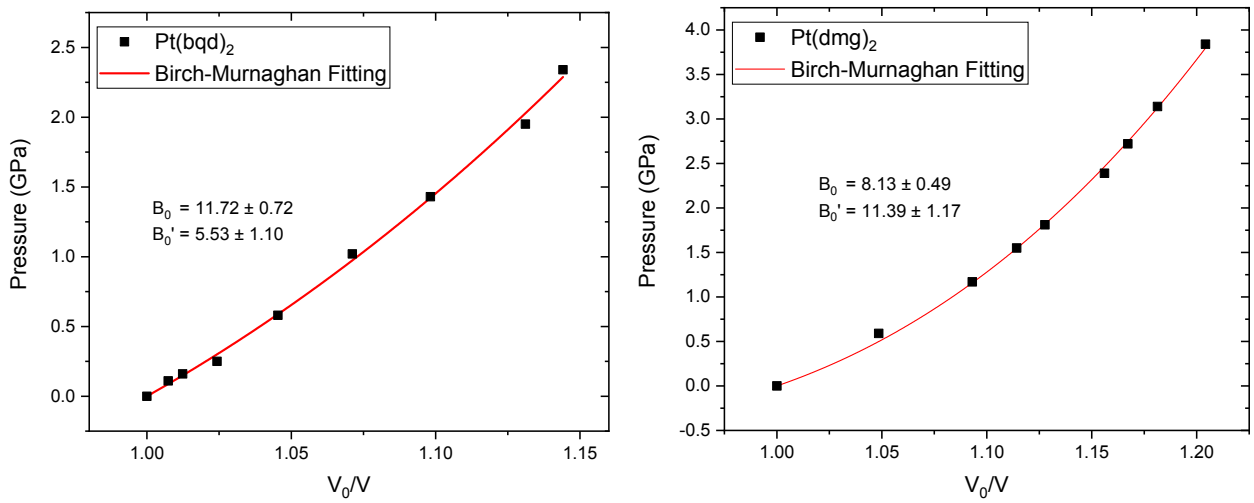


Figure S1: Pressure vs unit cell volume ratio (initial over current) for LEFT: $Pt(bqd)_2$ and RIGHT: $Pt(dmg)_2$. The lines in red show the Birch-Murnaghan fitting, with the bulk modulus (B_0) and it's derivative (B_0')

High pressure conductivity

Diamond anvil cell (DAC) apparatus

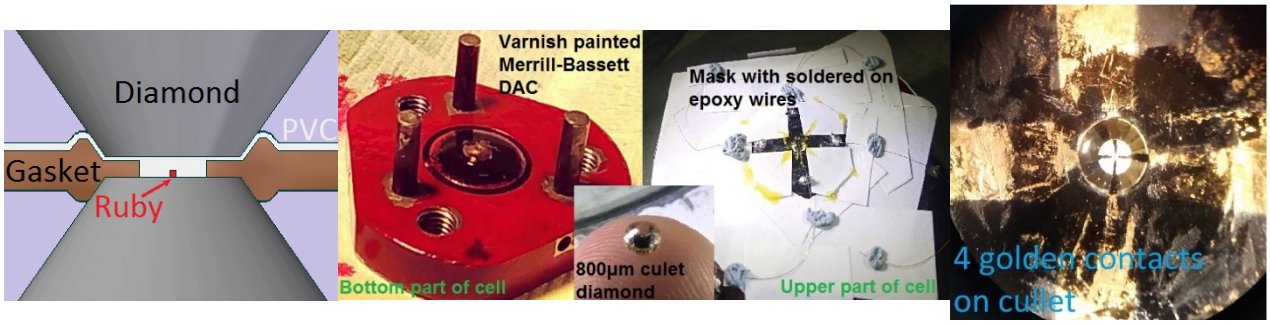


Figure S2: *Construction of gold contacts on diamond culet of DAC.*

Band gap determination – piston cylinder cell

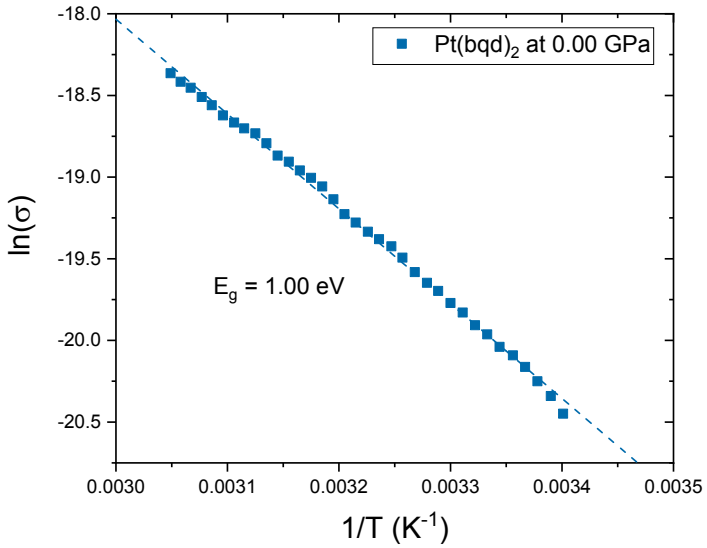


Figure S3: Plot of ln of conductivity vs 1/T at 0.00 GPa, showing semiconductor behaviour. The band gap E_g is determined as follows:

$$\ln \sigma = \frac{-E_g}{2kT}$$

Isolated molecule calculations on $Pt(bqd)_2$ and $Pt(dmg)_2$

Table S3: *MO energies and % MO contributions from key groups for $Pt(bqd)_2$. 'Chelate' refers to the N,O, H and C atoms involved around the Pt centre. 'Rest of ligand' includes any other atoms that are not part of the chelate.*

MO	Energy / eV	Pt	Chelate	'Rest of ligand'
L+4	-0.09	1	44	55
L+3	-0.38	14	25	61
L+2	-0.80	51	46	3
L+1	-2.73	9	54	38
LUMO	-3.58	6	65	29
HOMO	-5.56	11	62	27
H-1	-5.88	0	71	28
H-2	-7.03	2	96	3
H-3	-7.38	84	15	1
H-4	-7.65	25	40	34

Table S4: *MO energies and % MO contributions from key groups for $Pt(dmg)_2$. 'Chelate' refers to the N,O, H and C atoms involved around the Pt centre. 'Rest of ligand' includes any other atoms that are not part of the chelate.*

MO	Energy / eV	Pt	Chelate	'Rest of ligand'
L+4	0.45	64	1	38
L+3	-0.12	86	1	14
L+2	-0.41	52	44	4
L+1	-1.49	8	88	4
LUMO	-2.51	9	87	5
HOMO	-5.84	13	84	3
H-1	-6.02	0	97	3
H-2	-6.54	2	95	3
H-3	-7.03	76	23	1
H-4	-7.43	45	46	8

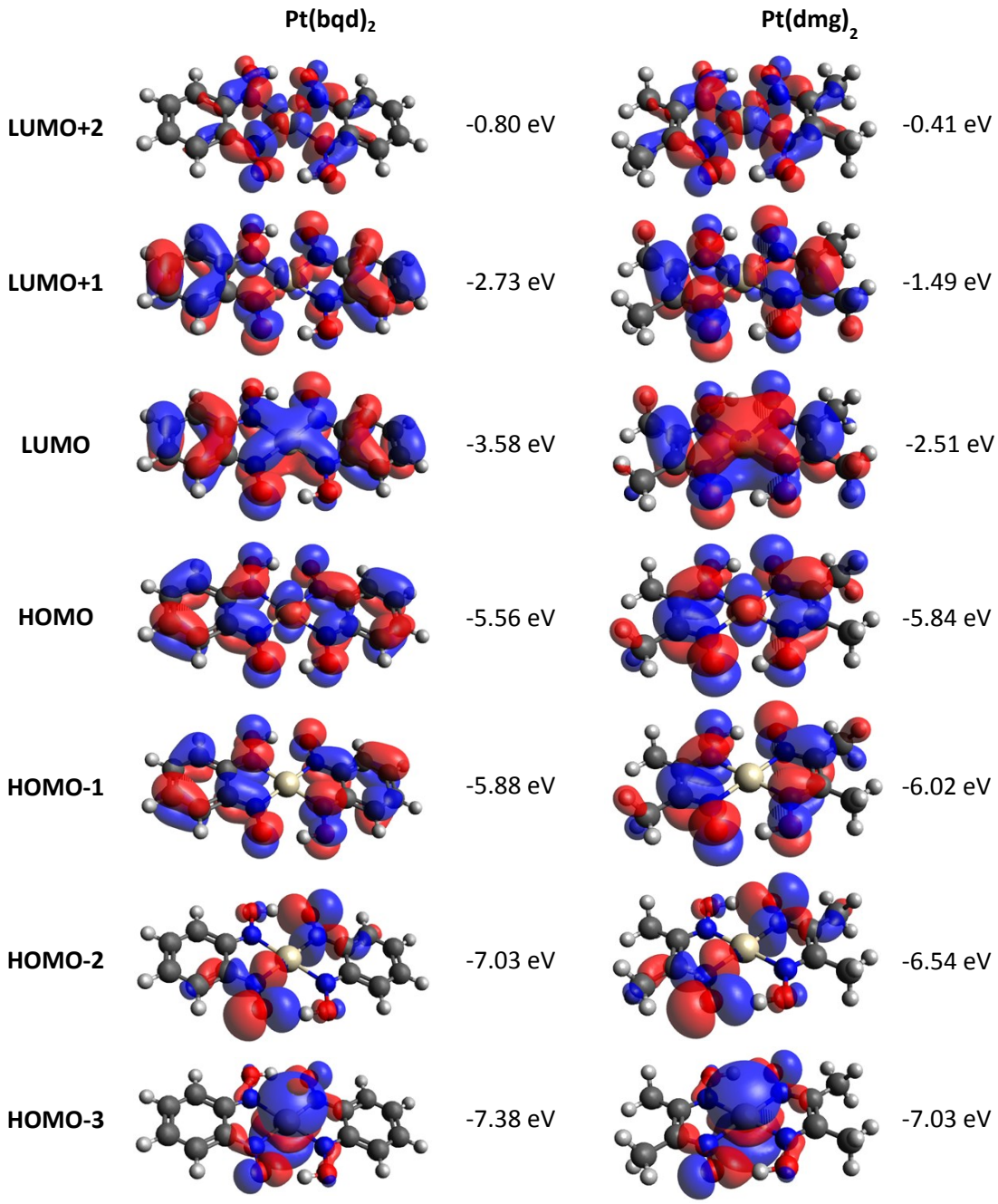
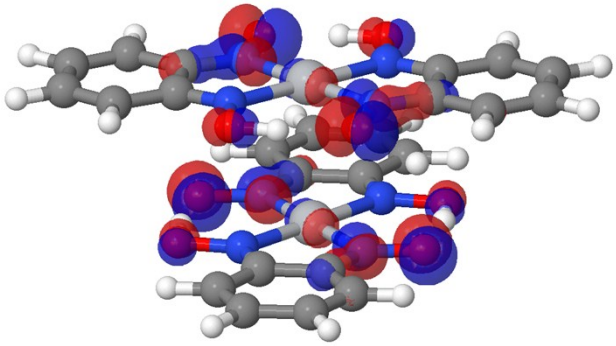
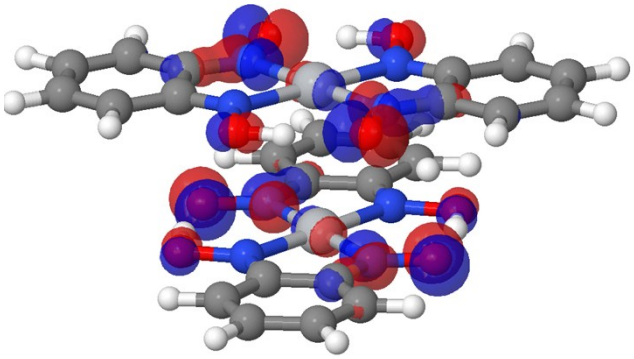


Figure S4: *Frontier molecular orbitals of $Pt(bqd)_2$ and $Pt(dmg)_2$ (isocontour value of 0.02100). Energies of the MOs shifted such that the HOMO sits at 0.00 eV.*

Visualisation of crystalline orbitals of $Pt(bqd)_2$



HOCO-6



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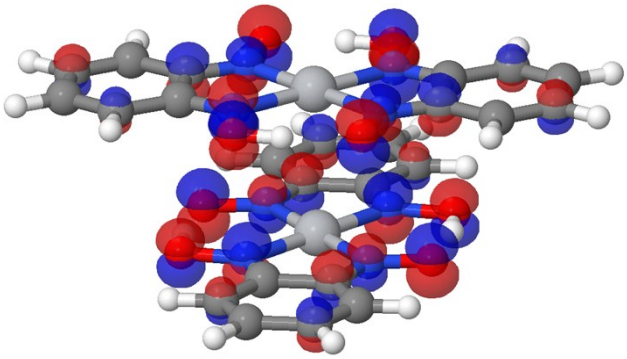

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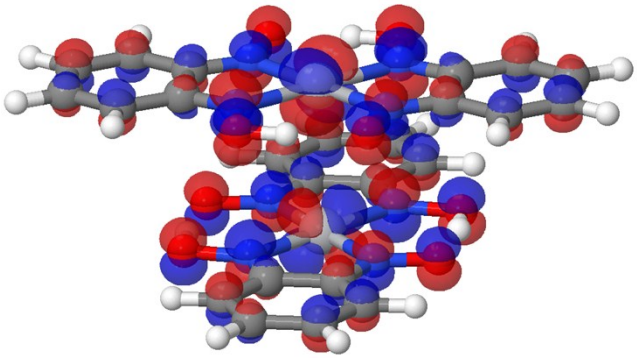

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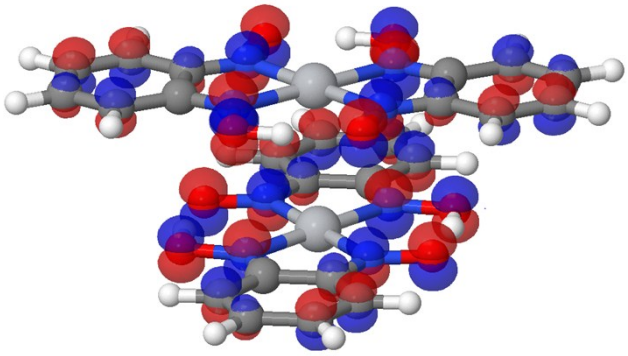

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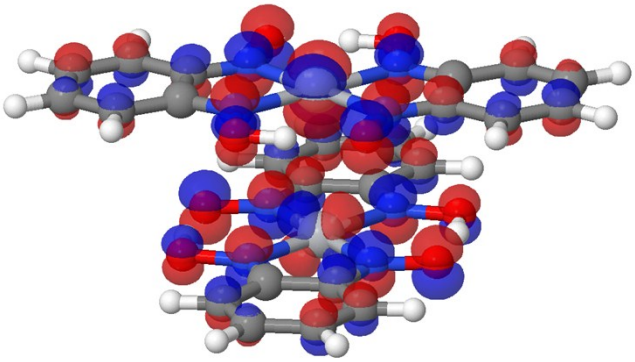

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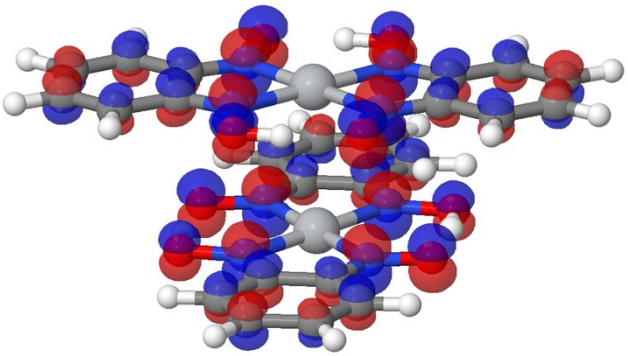

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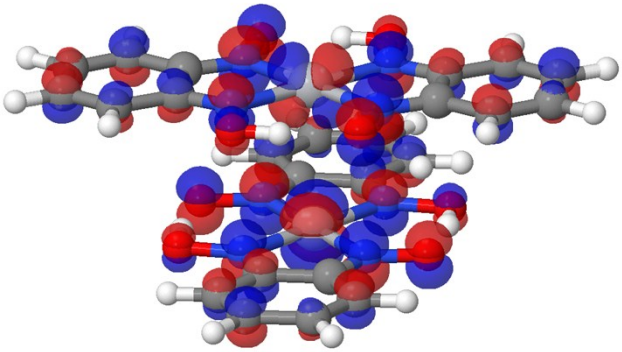

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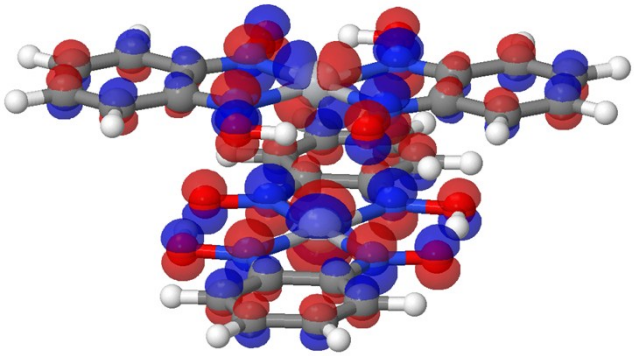

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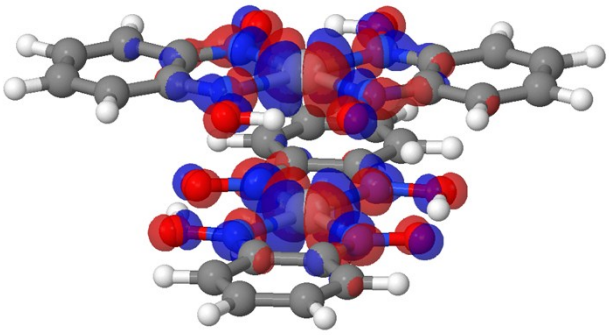

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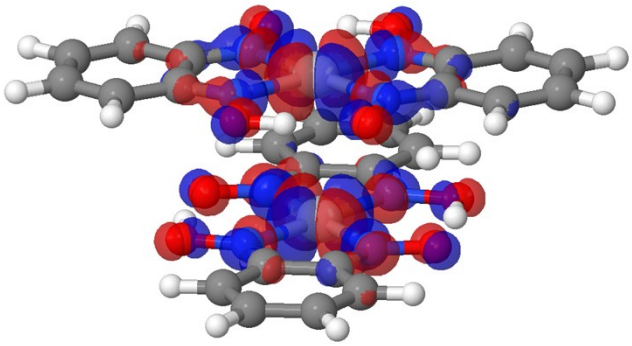
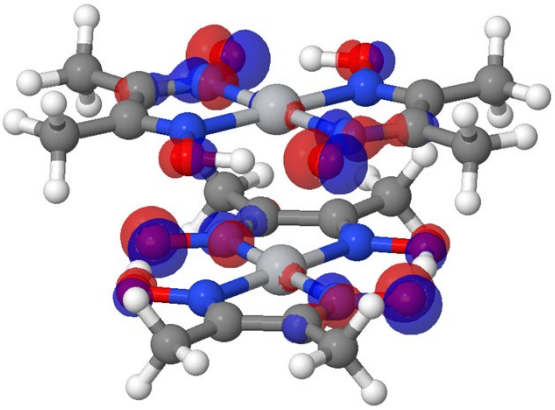


LUCO+5

Figure S5: Visualisation of frontier crystalline orbitals of $Pt(bqd)_2$ at the Γ point, at ambient pressure. The atoms are coloured as follows: white = H, dark grey = C, red = O, purple = N, light grey = Pt.

Visualisation of crystalline orbitals of $Pt(dmg)_2$



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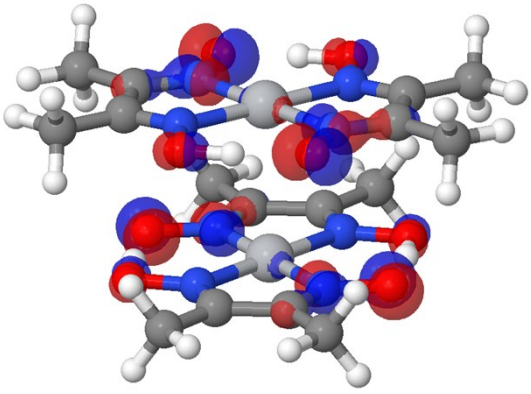

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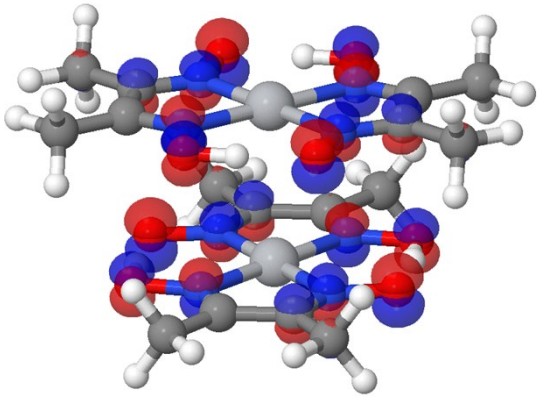

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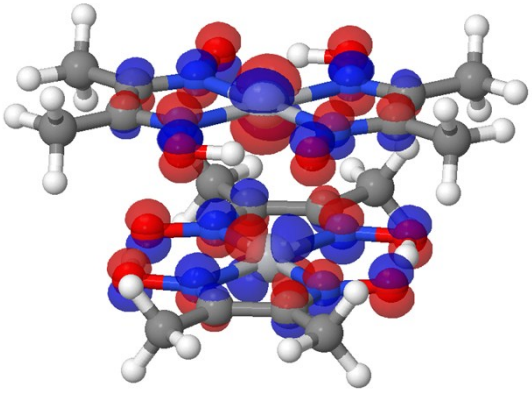

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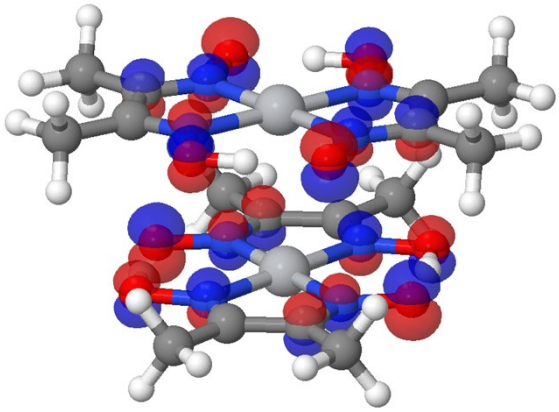

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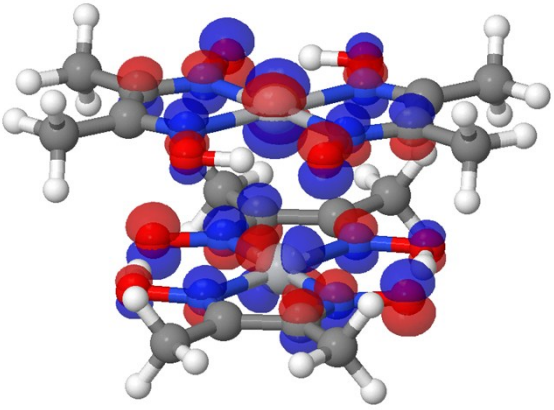

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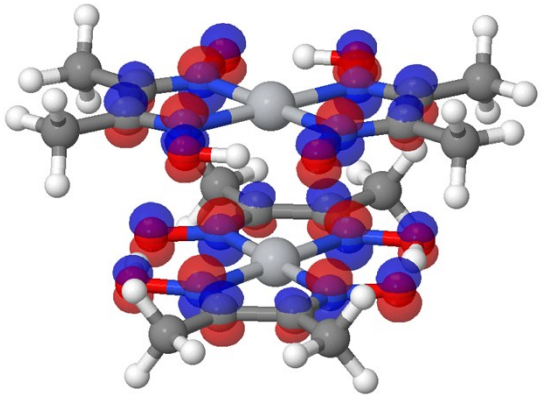

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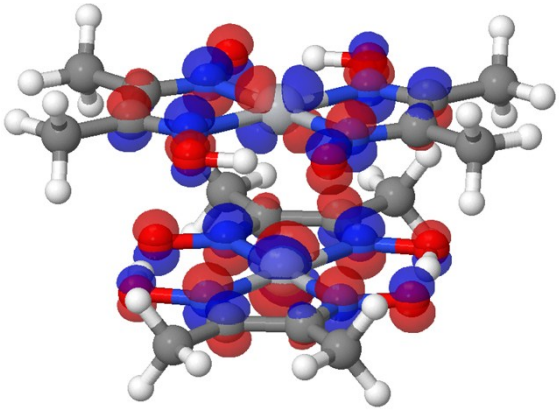

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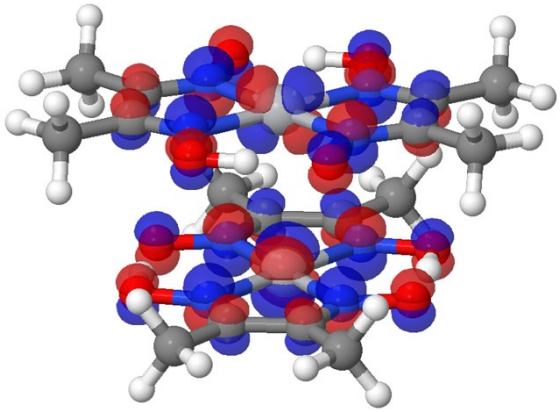

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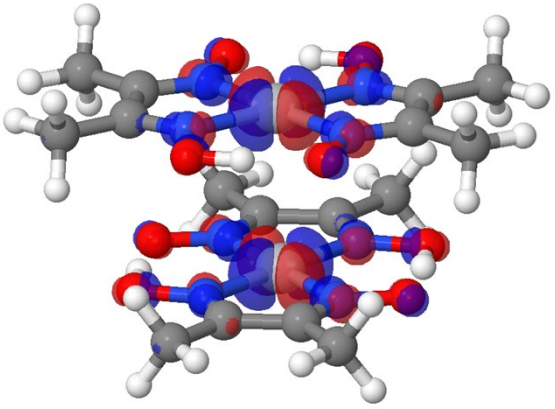

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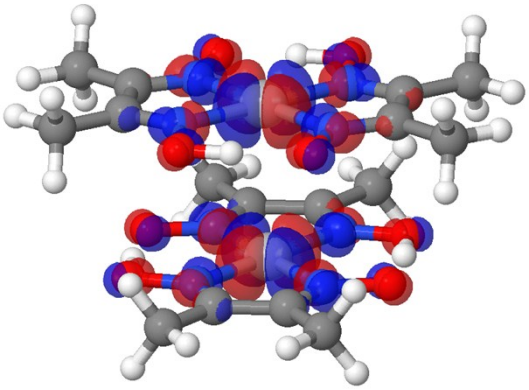

LUCO+5

Figure S6: Visualisation of frontier crystalline orbitals of $Pt(dmg)_2$ at the Γ point, at ambient pressure. The atoms are coloured as follows: white = H, dark grey = C, red = O, purple = N, light grey = Pt.

Band structure and PDOS plots for $Pt(bqd)_2$ at elevated pressures

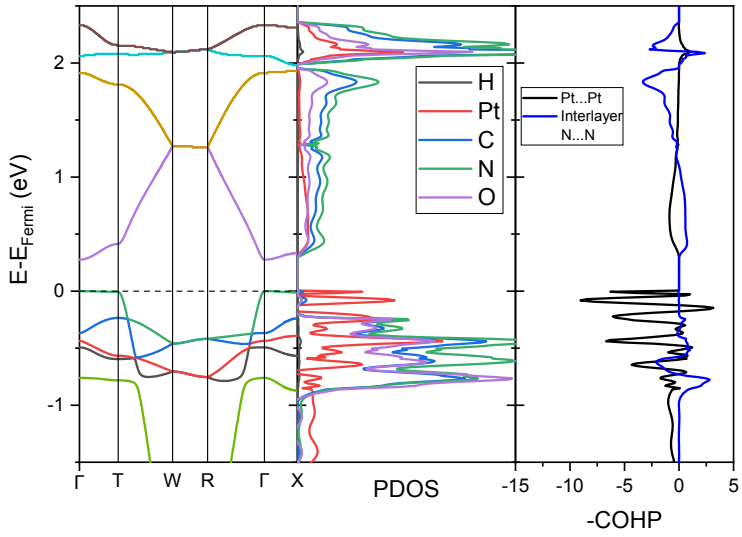

Figure S7: Computed band structure and PDOS for $Pt(bqd)_2$, broken down onto atomic contributions, at 0.29 GPa. The Fermi energy is set at 0 eV (dashed line, E_{Fermi} = -4.86 eV).

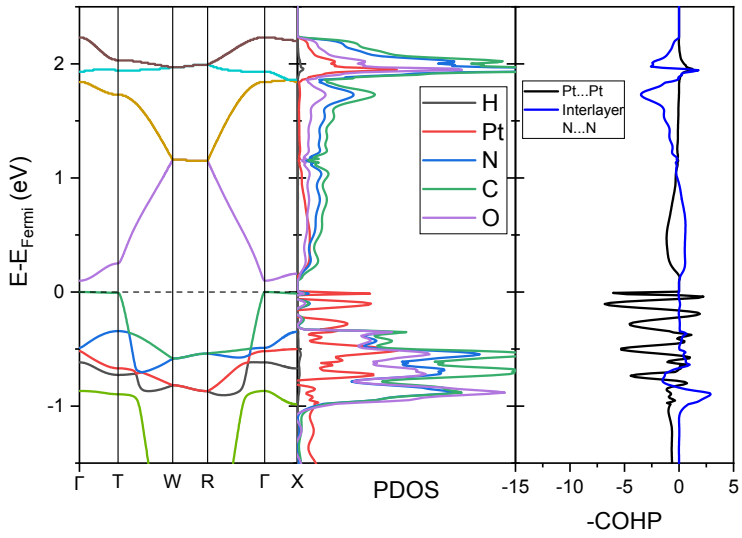

Figure S8: Computed band structure and PDOS for $Pt(bqd)_2$, broken down onto atomic contributions, at 0.58 GPa. The Fermi energy is set at 0 eV (dashed line, E_{Fermi} = -4.75 eV).

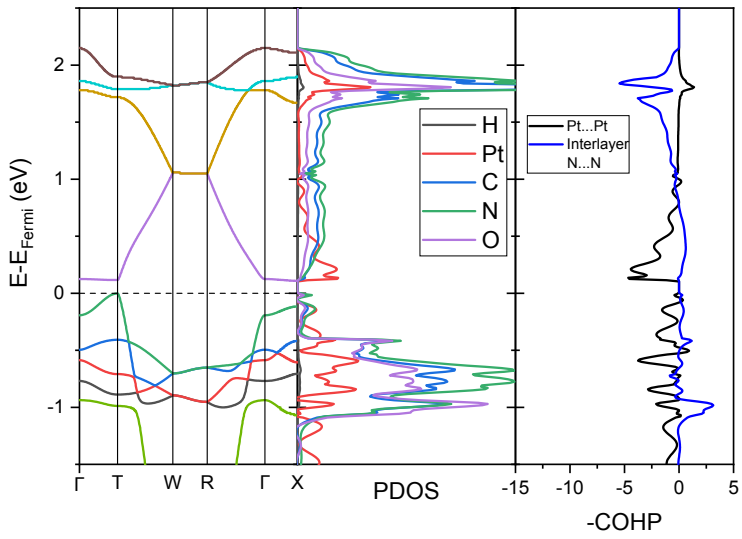

Figure S9: Computed band structure and PDOS for Pt(bqd)$_2$, broken down onto atomic contributions, at 1.47 GPa. The Fermi energy is set at 0 eV (dashed line, E_{Fermi} = -4.67 eV).

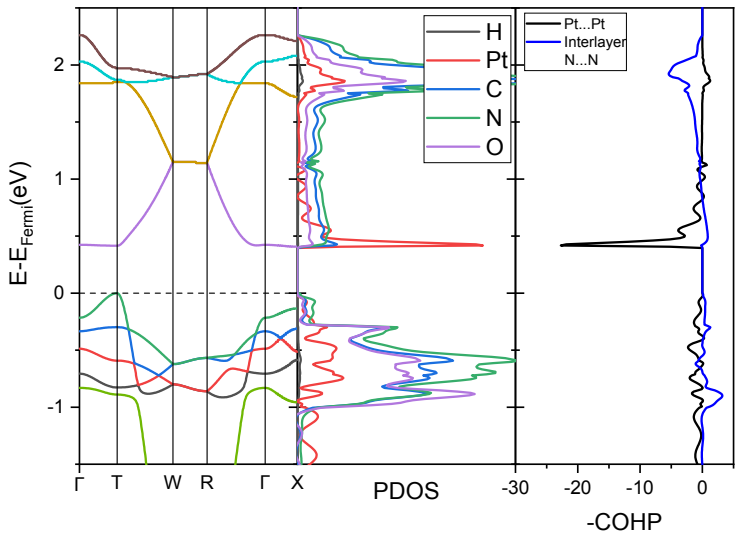

Figure S10: Computed band structure and PDOS for Pt(bqd)$_2$, broken down onto atomic contributions, at 1.98 GPa. The Fermi energy is set at 0 eV (dashed line, E_{Fermi} = -4.76 eV).

Computational Methodology - CRYSTAL17 calculations

Atom only calculations

Table S5: *Band gap from atom-only geometry optimisations with different functionals*

Functional	Calculated bandgap from 'atom only' optimisation (eV)
B3PW	0.762
B3LYP	0.785
PBE	0.000
PBE0	1.022
HSE06	0.518

Comparison of experimental structures to those obtained under 'atom-only' geometry optimisation

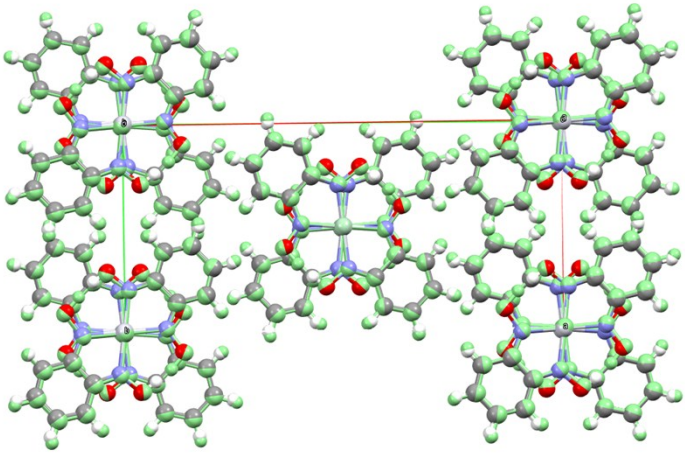

***Figure S11*:** Experimental structure (coloured by element) vs atom-only geometry optimised structure (green) for 0 GPa.

Table S6: *Bond lengths for experimental structure vs atom-only geometry optimised structure at 0 GPa.*

	Crystal 0 GPa		Functional		
Bond	σ		HSE06 0 Gpa	% change	Within 3σ?
Pt - N1	1.986	0.01	1.9781	-0.39778	TRUE
Pt - N2	1.987	0.011	2.0001	0.659285	TRUE
N1 - O1	1.338	0.016	1.398	4.484305	FALSE
N1 - C1	1.328	0.019	1.3075	-1.54367	TRUE
C1 - C2	1.44	0.002	1.4204	-1.36111	FALSE
C2 - C3	1.35	0.003	1.3504	0.02963	TRUE
C3 -C4	1.43	0.003	1.4304	0.027972	TRUE
C4 - C5	1.33	0.003	1.3479	1.345865	FALSE
C5 - C6	1.43	0.002	1.4198	-0.71329	FALSE
C6 - N2	1.33	0.002	1.3251	-0.36842	TRUE
N2 - O2	1.327	0.017	1.314	-0.97965	TRUE
C1 - C6	1.44	0.002	1.4591	1.326389	FALSE
Average				0.209126	

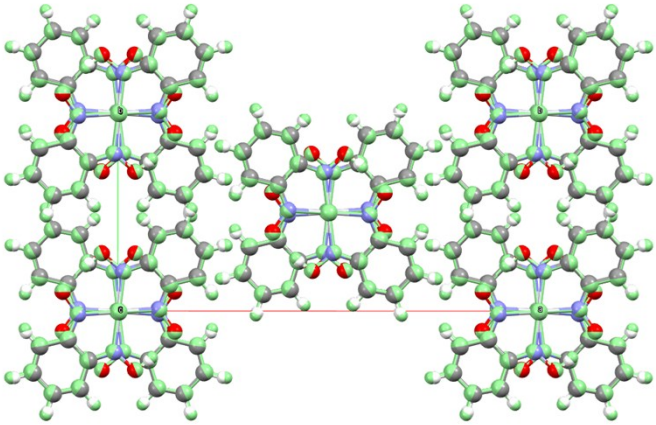

Figure S12: *Experimental structure (coloured by element) vs atom-only geometry optimised structure (green) for 0.29 GPa*

Table S7: *Bond lengths for experimental structure vs atom-only geometry optimised structure at 0.29 GPa.*

	Crystal 0.29 GPa		Functional		
Bond		σ	HSE06 0.29 Gpa	% change	Within 3σ?
Pt - N1	1.994	0.009	1.9775	-0.82748	TRUE
Pt - N2	1.981	0.019	1.999	0.908632	TRUE
N1 - O1	1.34	0.002	1.3936	4.000000	FALSE
N1 - C1	1.33	0.002	1.307	-1.72932	FALSE
C1 - C2	1.441	0.016	1.4212	-1.37405	TRUE
C2 - C3	1.35	0.003	1.3494	-0.04444	TRUE
C3 -C4	1.42	0.003	1.4324	0.873239	FALSE
C4 - C5	1.33	0.002	1.3476	1.323308	FALSE
C5 - C6	1.43	0.003	1.4188	-0.78322	FALSE
C6 - N2	1.332	0.017	1.3224	-0.72072	TRUE
N2 - O2	1.33	0.002	1.3192	-0.81203	FALSE
C1 - C6	1.44	0.002	1.4586	1.291667	FALSE
Average				0.175465	

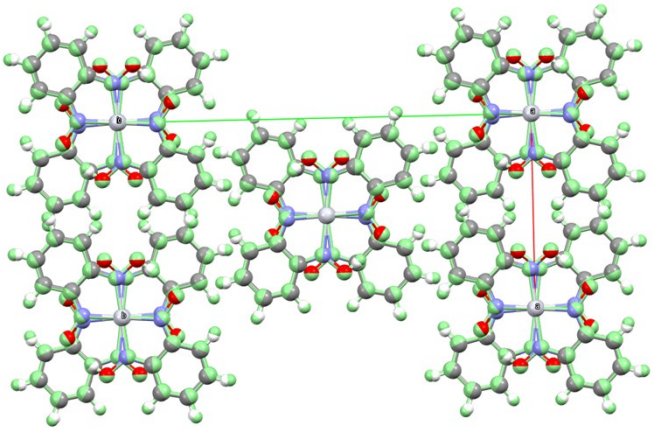

Figure S13: *Experimental structure (coloured by element) vs atom-only geometry optimised structure (green) for 0.58 GPa*

Table S8: *Bond lengths for experimental structure vs atom-only geometry optimised structure at 0.58 GPa.*

	Crystal 0.58 GPa		Functional		
Bond	σ		HSE06 0.58 Gpa	% change	Within 3σ?
Pt - N1	1.977	0.007	1.9762	-0.04047	TRUE
Pt - N2	1.957	0.014	1.9979	2.089934	TRUE
N1 - O1	1.336	0.019	1.3925	4.229042	TRUE
N1 - C1	1.33	0.002	1.307	-1.72932	FALSE
C1 - C2	1.444	0.013	1.4205	-1.62742	TRUE
C2 - C3	1.34	0.003	1.3494	0.701493	FALSE
C3 -C4	1.42	0.002	1.4321	0.852113	FALSE
C4 - C5	1.331	0.017	1.3478	1.262209	TRUE
C5 - C6	1.43	0.02	1.4184	-0.81119	TRUE
C6 - N2	1.333	0.015	1.322	-0.82521	TRUE
N2 - O2	1.331	0.019	1.3198	-0.84147	TRUE
C1 - C6	1.435	0.017	1.4582	1.616725	TRUE
Average				0.40637	

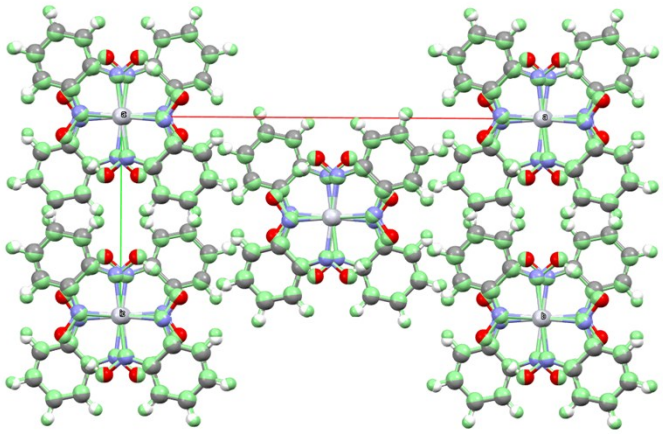

Figure S14: *Experimental structure (coloured by element) vs atom-only geometry optimised structure (green) for 1.03 GPa.*

Table S9: *Bond lengths for experimental structure vs atom-only geometry optimised structure at 1.03 GPa.*

	Crystal 1.03 Gpa		Functional		
Bond		σ	HSE06	% change	Within 3σ?
Pt - N1	2.002	0.01	1.975	-1.34865	TRUE
Pt - N2	2.04	0.002	1.9965	-2.13235	FALSE
N1 - O1	1.34	0.002	1.3914	3.835821	FALSE
N1 - C1	1.33	0.003	1.3072	-1.71429	FALSE
C1 - C2	1.441	0.016	1.4191	-1.51978	TRUE
C2 - C3	1.35	0.003	1.3495	-0.03704	TRUE
C3 -C4	1.42	0.003	1.4312	0.788732	FALSE
C4 - C5	1.33	0.002	1.3481	1.360902	FALSE
C5 - C6	1.43	0.003	1.4175	-0.87413	FALSE
C6 - N2	1.333	0.017	1.3219	-0.83271	TRUE
N2 - O2	1.33	0.002	1.3203	-0.72932	FALSE
C1 - C6	1.44	0.002	1.457	1.180556	FALSE
Average				-0.16852	

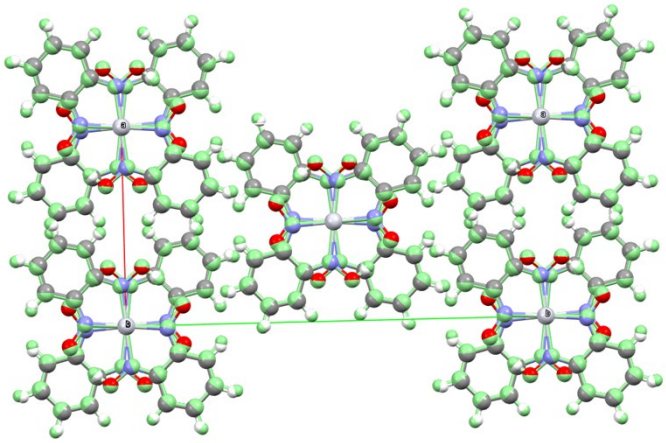

Figure S15: *Experimental structure (coloured by element) vs atom-only geometry optimised structure (green) for 1.47 GPa.*

Table S10: *Bond lengths for experimental structure vs atom-only geometry optimised structure at 1.47 GPa.*

	Crystal 1.47 Gpa		Functional		
Bond		σ	HSE06 1.47 Gpa	% change	Within 3σ?
Pt - N1	1.988	0.016	1.9741	-0.6992	TRUE
Pt - N2	1.99	0.003	1.9943	0.21608	TRUE
N1 - O1	1.34	0.004	1.39	3.731343	FALSE
N1 - C1	1.33	0.004	1.3081	-1.64662	FALSE
C1 - C2	1.44	0.002	1.4177	-1.54861	FALSE
C2 - C3	1.35	0.005	1.35	0	TRUE
C3 -C4	1.42	0.004	1.4295	0.669014	TRUE
C4 - C5	1.34	0.003	1.3489	0.664179	TRUE
C5 - C6	1.42	0.004	1.4164	-0.25352	TRUE
C6 - N2	1.33	0.003	1.3224	-0.57143	TRUE
N2 - O2	1.33	0.004	1.3213	-0.65414	TRUE
C1 - C6	1.44	0.004	1.4555	1.076389	FALSE
Average				0.081958	

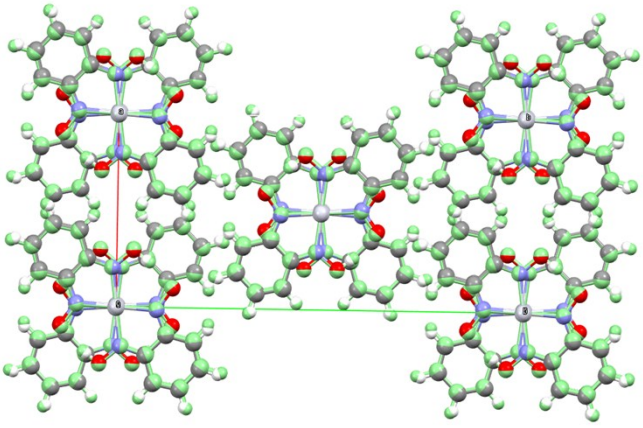

Figure S16: *Experimental structure (coloured by element) vs atom-only geometry optimised structure (green) for 1.98 GPa*

Table S11: *Bond lengths for experimental structure vs atom-only geometry optimised structure at 1.98 GPa.*

	Crystal 1.98 Gpa		Functional		
Bond		σ	HSE06 1.98 Gpa	% change	Within 3σ?
Pt - N1	1.964	0.017	1.9721	0.412424	TRUE
Pt - N2	2.01	0.004	1.9921	-0.89055	FALSE
N1 - O1	1.34	0.004	1.3883	3.604478	FALSE
N1 - C1	1.33	0.005	1.3083	-1.63158	FALSE
C1 - C2	1.44	0.002	1.416	-1.66667	FALSE
C2 - C3	1.35	0.005	1.35	0	TRUE
C3 -C4	1.42	0.005	1.4282	0.577465	TRUE
C4 - C5	1.33	0.004	1.3493	1.451128	FALSE
C5 - C6	1.42	0.005	1.4151	-0.34507	TRUE
C6 - N2	1.33	0.003	1.3222	-0.58647	TRUE
N2 - O2	1.33	0.004	1.3221	-0.59398	TRUE
C1 - C6	1.44	0.004	1.454	0.972222	FALSE
Average				0.108617	

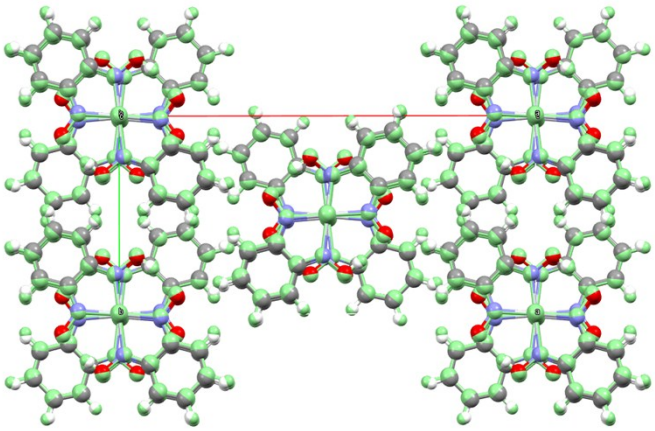

Figure S17: *Experimental structure (coloured by element) vs atom-only geometry optimised structure (green) for 2.38 GPa.*

Table S12: *Bond lengths for experimental structure vs atom-only geometry optimised structure at 2.38 GPa.*

	Crystal 2.38 Gpa		Functional		
Bond		σ	HSE06 2.38 Gpa	% change	Within 3σ?
Pt - N1	1.972	0.017	1.9714	-0.03043	TRUE
Pt - N2	2.000	0.004	1.9909	-0.455	TRUE
N1 - O1	1.340	0.004	1.3877	3.559701	FALSE
N1 - C1	1.330	0.005	1.3083	-1.63158	FALSE
C1 - C2	1.440	0.003	1.4154	-1.70833	FALSE
C2 - C3	1.360	0.006	1.35	-0.73529	TRUE
C3 -C4	1.430	0.005	1.4277	-0.16084	TRUE
C4 - C5	1.330	0.004	1.3494	1.458647	FALSE
C5 - C6	1.440	0.004	1.4145	-1.77083	FALSE
C6 - N2	1.330	0.003	1.322	-0.6015	TRUE
N2 - O2	1.330	0.004	1.3222	-0.58647	TRUE
C1 - C6	1.440	0.004	1.4533	0.923611	FALSE
Average				-0.14486	

Table S13: *RMS difference between the experimental and atom-only geometry optimised structures.*

Pressure (GPa)	RMS
0	0.148
0.29	0.031
0.58	0.049
1.03	0.083
1.47	0.058
1.98	0.062
2.38	0.072

References

(1) Montgomery, H. C. Method for Measuring Electrical Resistivity of Anisotropic Materials. *J. Appl. Phys.* **1971**, *42* (7), 2971–2975. https://doi.org/10.1063/1.1660656.