Review

Putting the Squeeze on Molecule-Based Magnets: Exploiting Pressure to Develop Magneto-Structural Correlations in Paramagnetic Coordination Compounds

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Received: 20 July 2020; Accepted: 10 August 2020; Published: 12 August 2020

Abstract: The cornerstone of molecular magnetism is a detailed understanding of the relationship between structure and magnetic behaviour, i.e., the development of magneto-structural correlations. Traditionally, the synthetic chemist approaches this challenge by making multiple compounds that share a similar magnetic core but differ in peripheral ligation. Changes in the ligand framework induce changes in the bond angles and distances around the metal ions, which are manifested in changes to magnetic susceptibility and magnetisation data. This approach requires the synthesis of a series of different ligands and assumes that the chemical/electronic nature of the ligands and their coordination to the metal, the nature and number of counter ions and how they are positioned in the crystal lattice, and the molecular and crystallographic symmetry have no effect on the measured magnetic properties. In short, the assumption is that everything outwith the magnetic core is inconsequential, which is a huge oversimplification. The ideal scenario would be to have the same complex available in multiple structural conformations, and this is something that can be achieved through the application of external hydrostatic pressure, correlating structural changes observed through high-pressure single crystal X-ray crystallography with changes observed in high-pressure magnetometry, in tandem with high-pressure inelastic neutron scattering (INS), high-pressure electron paramagnetic resonance (EPR) spectroscopy, and high-pressure absorption/emission/Raman spectroscopy. In this review, which summarises our work in this area over the last 15 years, we show that the application of pressure to molecule-based magnets can (reversibly) (1) lead to changes in bond angles, distances, and Jahn–Teller orientations; (2) break and form bonds; (3) induce polymerisation/depolymerisation; (4) enforce multiple phase transitions; (5) instigate piezochromism; (6) change the magnitude and sign of pairwise exchange interactions and magnetic anisotropy, and (7) lead to significant increases in magnetic ordering temperatures.

Keywords: high pressure X-ray crystallography; high pressure magnetometry; high pressure absorption spectroscopy; molecule-based magnets; single-molecule magnets; single-ion magnets
1. Introduction

Over the last 50 years, there has been a significant increase in the number of high-pressure single-crystal and powder diffraction studies performed on molecular systems, with several comprehensive reviews on the subject, including the effect of pressure on amino acids [1], metal complexes [2] and metal–organic frameworks [3,4]. The complexity of molecular systems examined under pressure has grown significantly with the first molecules consisting of just a handful of atoms, such as benzene, which was first published in 1969 [5]. More recently, molecular porous systems containing thousands of atoms and with unit cell volumes in excess of 55,000 Å\(^3\) have been studied (Figure 1) [6]. In all, some 3328 structures in the Cambridge Structural Database (CSD) have been collected at pressure to date (CSD version 5.41).

Advances in pressure cell technology, and in particular the size and ease of use of diamond anvil cells (DACs) such as the Merrill Bassett cell [7], turnbuckle cell [8], and other miniature diamond anvil cells [9] has made possible the study of molecular systems of increasing complexity. One area where the use of pressure has seen a significant rise in popularity is in the study of functional materials where high-pressure diffraction studies performed in conjunction with other high-pressure measurements on the same sample have helped develop structure–property relationships. Supplementary techniques have included high-pressure UV-Vis [10], fluorescence emission [11], conductivity [12], Mössbauer [13], and magnetic measurements. These combined studies have revealed how structural distortions, caused by increasing pressure, have enforced changes in the physical properties of materials. Examples include measuring changes in conductivity and band structure in molecular conductors [12], monitoring framework ‘breathing effects’ on the uptake of guest species within porous metal–organic framework materials [14], and how structural changes in encapsulated fluorophores affect emission properties [11]. One area where this approach has made a significant impact is in the field of magnetism. Herein, we highlight our efforts in developing magneto-structural correlations in transition metal molecule-based magnets; we do not attempt to cover examples from other researchers, which are many and varied [15–31]. At the outset, what we hoped to observe was that applied pressure would change bond lengths and angles around the metal centres, and that that would lead to changes in magnetic exchange interactions and/or magneto-anisotropies. Our reasons for choosing particular complexes to study were, at least initially, influenced by those whose ambient structure–property relations had been well established in the literature. Some came from our own back catalogue of compounds, the structures and physical properties of which we understood well. All exchange interactions (\(J\)) in this review are quoted in the \(H = \Sigma -2J_{ij}S_iS_j\) formalism.
2. Mn Complexes

The compounds we chose to study first were those containing Mn\(^{\text{III}}\). This was for a number of reasons. At the beginning of our combined research efforts in 2006, we were making Mn\(^{\text{III}}\)-based Single-Molecule Magnets (SMMs) and had a large library of complexes from which to choose, many of which had very interesting structural/magnetic features [32,33]. Aligned to this was the presence of the Jahn–Teller (JT) axis of the octahedral Mn\(^{\text{III}}\) ion. Given the well-known dynamic JT effect observed in numerous coordination compounds [34], we speculated that hydrostatic pressure would be capable of changing JT bond lengths/orientations, and that that would have a pronounced effect on both magnetic exchange interactions and magnetic anisotropy.

The compounds [Mn\(_6\)O\(_2\)(Et-sao)\(_6\)(O\(_2\)C-Ph(Me)\(_2\))\(_2\)(EtOH)\(_6\)] (1) and [Mn\(_6\)O\(_2\)(Et-sao)\(_8\)(O\(_2\)C-naphth)\(_2\)(EtOH)\(_4\)(H\(_2\)O)\(_2\)] (2; sao\(^{2-}\) is the dianion of salicylaldoxime) are part of a well-studied family of SMMs for which detailed magneto-structural correlations under ambient conditions have been developed [35–37]. The general structure of these complexes (Figure 2) describes two parallel, off-set [Mn\(^{\text{III}}\)\(_3\)(\(\mu_3\)-O)]\(^{2+}\) triangular subunits linked via two central oximate O-atoms and two peripheral phenoxide O-atoms, leading to a [Mn\(^{\text{III}}\)\(_6\)(\(\mu_3\)-O)\(_2\)(\(\mu_3\)-ONR)\(_2\)(\(\mu\)-ONR)\(_4\)]\(^{8+}\) core. The bridging between neighbouring Mn ions within each triangle occurs through an NO oximate group, such that each Mn\(_2\) pair forms a −Mn−N−O−Mn− moiety, and thus the Mn\(_3\) triangle, a (−Mn−O−N−)\(_3\) ring. The coordination spheres of the Mn ions are completed by two terminal carboxylates (one on each triangle) and by terminal solvent molecules. All Mn ions are in the 3+ oxidation state and are six-coordinate adopting distorted (pseudo) octahedral geometry, with their axially elongated JT axes approximately perpendicular to the [Mn\(_3\)O]\(^{2+}\) planes [38]. All family members can be categorised into two subsections according to their magnetic behaviour: those possessing intra-triangle antiferromagnetic exchange interactions, and those possessing intra-triangle ferromagnetic exchange interactions. All family members display inter-triangle ferromagnetic exchange. This results in compounds with \(S = 12\) ground states in the latter and \(4 \leq S < 12\) ground states in the former. Interestingly, the sign and magnitude of the magnetic exchange is controlled through R-saoH\(_2\) ligand design, with larger, non-rigid R (in the main, e.g., R = Me, Et) causing puckering of the −Mn−N−O−Mn− moiety. The change in torsion angle from near planar (when R = H for example) to non-planar decreases the antiferromagnetic contribution to the nearest-neighbour exchange, and at approximately 31°, the pairwise interaction switches to being ferromagnetic [39]. Given that such enormous changes in magnetic behaviour are observed through very small changes in structure, aligned to the fact that the magnitude of the exchange (\(J\)) is very small (and thus the absolute difference in \(J\) is small) made compounds 1 and 2 ideal candidates for the first ever combined HP single crystal X-ray diffraction/HP magnetic study of a SMM.

![Figure 2](image_url)

**Figure 2.** (a) The molecular structure of complex 1. (b) The molecular structure of complex 2. (c) The metallic skeleton common to 1 and 2. Colour code: Mn = lilac, O = red, N = blue, C = grey. H atoms are omitted for clarity.
Hydrostatic high-pressure (HP) single-crystal X-ray diffraction (XRD) measurements were
performed on 1 and 2 in petroleum ether at \( T = 300 \text{ K} \) to a maximum pressure of 1.5 GPa [40].
1 and 2 crystallise in the monoclinic space groups \( P2_1/n \) and \( P2_1/c \), respectively, and remain so in the full
pressure range. The most obvious initial effect for both is a compression of the unit cell, by approximately
6.5% (1) and 10% (2), which is assigned to a reduction of void space given the lack of significant intermolecular
interactions (H-bonds or \( \pi-\pi \) stacking). The closest intermolecular interactions (H···H)
reduce by a maximum of approximately 0.9 Å in 1 and just 0.07 Å in 2. The intramolecular changes
are more remarkable (Figure 3), with the Mn–N–O–Mn torsion angles flattened considerably, and the
JT axes compressing and re-aligning differently with respect to the plane of the three metal centres
in the triangle (Tables 1 and 2). The Mn–N–O–Mn torsion angles decrease by up to approximately
5.1° (1), 5.7° (2). Significantly, the Mn1–N–O–Mn3 torsion angle in both cases falls from above to
below the angle expected to switch the pairwise exchange from ferromagnetic to antiferromagnetic;
34.8(5)→29.7(11)° (1), 33.2(2)→27.5(17)° (2). Note that Mn3 lies at the periphery of the molecule, away
from the more structurally rigid core, and it is the only metal ion bonded to two solvent molecules,
which sit on its JT axis. The changes in the JT axes with pressure are less consistent. For 1, the JT axes
of Mn1 and Mn2 are compressed with pressure (2.132(2), 2.434(3) Å → 2.095(5), 2.359(5) Å; 2.196(3),
2.480(3) Å → 2.151(6), 2.423(7) Å, respectively). However, the JT of Mn3 actually elongates at 0.5 GPa,
before compressing at all other (higher) pressures, resulting in a small overall compression of one
bond and a small overall elongation of the other. All three JT axes move to become slightly more
perpendicular to the mean plane of the [Mn3] triangle, albeit by just approximately 0.9–1.6°. In 2,
the JT axes all compress with pressure (Mn1, 2.102(3), 2.508(3) Å → 2.033(7), 2.486(9) Å; Mn2, 2.205(3),
2.397(3) Å → 2.141(9), 2.387(11) Å; Mn3, 2.395(3), 2.188(3) Å → 2.398(7), 2.107(7) Å) and variations in
the alignment of the axes are within the statistical error, although the trend appears analogous to that
seen for 1.

Figure 3. Comparison of Jahn–Teller bond lengths and Mn–O–N–Mn torsion angles in 1 at (a) ambient
pressure and (b) 1.5 GPa. Colour code as Figure 1.
Table 1. Comparison of the Mn–O–N–Mn torsion angles (°) at ambient pressure and at 1.5 GPa for complexes 1 and 2.

|                  | At Ambient Pressure in 1 | At 1.5 GPa in 1 | At Ambient Pressure in 2 | At 1.5 GPa in 2 |
|------------------|-------------------------|----------------|-------------------------|----------------|
| Mn1–O–N–Mn2°     | 43.0(2)                 | 42.2(10)       | 41.1(2)                 | 41.1(1.7)      |
| Mn2–O–N–Mn3°     | 39.1(2)                 | 34.6(11)       | 40.5(2)                 | 36.5(1.8)      |
| Mn3–O–N–Mn1°     | 34.8(5)                 | 29.7(11)       | 33.2(2)                 | 27.5(1.7)      |

Table 2. Comparison of the bond lengths (Å) of the Jahn–Teller axes at ambient pressure and at 1.5 GPa for complexes 1 and 2.

|                  | Mn1–O2/Å | Mn1–O92/Å | Mn2–O15/Å | Mn2–O11/Å | Mn3–O14/Å | Mn3–O124/Å |
|------------------|----------|-----------|-----------|-----------|-----------|------------|
| At ambient pressure in 1 | 2.132(2) | 2.434(3)  | 2.196(3)  | 2.480(3)  | 2.242(3)  | 2.333(3)   |
| At 1.5 GPa in 1     | 2.093(5) | 2.359(5)  | 2.151(6)  | 2.423(7)  | 2.279(6)  | 2.320(7)   |

|                  | Mn1–O24/Å | Mn1–O92/Å | Mn2–O15/Å | Mn2–O11/Å | Mn3–O17/Å | Mn3–O16/Å |
|------------------|-----------|-----------|-----------|-----------|-----------|-----------|
| At ambient pressure in 2 | 2.102(3) | 2.508(3)  | 2.205(3)  | 2.397(3)  | 2.395(3)  | 2.188(3)  |
| At 1.5 GPa in 2     | 2.033(7) | 2.486(9)  | 2.141(9)  | 2.387(11)| 2.398(7)  | 2.107(7)  |

HP susceptibility and magnetisation data were collected to 2 GPa using Daphne 7373 oil as the pressure transmitting medium. The magnetic behaviour of 1 and 2 at ambient pressure has been described in detail previously [32,41]. In the following text, the numbers in brackets refer to complex 2. Data measured in the cell, but with zero applied pressure (\(T = 300–5\) K, \(B = 0.1\) T), can be simulated with the parameters \(g = 1.99(2.03)\) and \(J = +1.75 (+1.31)\) cm\(^{-1}\) in a model assuming all exchange interactions are the same. With increasing pressure, the value of \(\chi M T\) increases more slowly with decreasing temperature and has a much smaller maximum for both complexes, which is clearly indicative of a weaker (less positive) ferromagnetic exchange interaction, and/or the presence of antiferromagnetic exchange. Indeed, simulation of the susceptibility data for 1 at the highest pressures measured requires the introduction of a 2\(J\) model in which the Mn1–Mn3 exchange interaction is antiferromagnetic \(J_1 = +1.10 (+1.00)\) cm\(^{-1}\), \(J_{\text{Mn1–Mn3}} = -0.10 (-0.45)\) cm\(^{-1}\), which is consistent with the structural changes in the torsion angles. Simulations suggest the spin ground state remains \(S = 12\) at lower pressures, but it switches to \(S = 11\) (or smaller) at higher pressures. A fit of the magnetisation data for compound 1 measured in the cell, but with zero applied pressure (\(T = 2–7\) K, \(B = 0.5–5.0\) T) to an axial zero-field splitting (zfs) plus Zeeman Hamiltonian (Giant Spin Model) affords \(S = 12, g = 1.99,\) and \(D = -0.38\) cm\(^{-1}\), which is consistent with that observed for all ferromagnetically coupled members of the family. At the highest pressures measured, these parameters become \(S = 11, g = 1.98,\) and \(D = -0.34\) cm\(^{-1}\). The data for 2 could not be fitted, but qualitatively show a similar trend in behaviour. As expected with decreasing \(|J|\) and the introduction of antiferromagnetic exchange, the barrier to magnetisation reversal in these SMMs is reduced dramatically (Figure 4). There is a clear pressure and frequency-dependent decrease in the out-of-phase, \(\chi'\), peak positions in the ac susceptibility data from \(T \leq 6\) K. For example, for 1, the peak at 300 Hz at 0(1.75) GPa occurs at approximately 6.3(4.8) K; for 2, the peak at 100 Hz at 0(1.4) GPa occurs at 3.9(3.0) K. A fit of the HP \(\chi'\) data to the Arrhenius equation revealed a decrease in \(U_{\text{eff}}\) in 1(2) from 83(63) K to 63(47) K. This is also manifested in the change in the appearance of the magnetisation hysteresis loops that show a clear reduction in coercivity with increased pressure (Figure 4).
Figure 4. (a) Arrhenius plots based on out-of-phase ac susceptibility measurements of 1 at different pressures. (b) Hysteresis loops for 1 recorded at the indicated pressures at 2 K.

The second SMM to be the focus of a combined HP crystallography/magnetism study was the compound \([\text{Mn}_3(\text{Hcht})_2(\text{bpy})_4](\text{ClO}_4)_3\cdot\text{Et}_2\text{O}·2\text{MeCN}\) (3-\text{Et}_2\text{O}·2\text{MeCN}; \text{Hcht}^{2-} is the dianion of cis, cis-1,3,5-cyclohexanetriol and bpy is 2,2’-bipyridine) [42,43]. The structure of 3 (Figure 5) contains a linear \([\text{Mn}^{III}_3\text{Mn}^{II}_2\text{O}_4]^{3+}\) core with the central \(\text{Mn}^{III}\) centre (Mn1) bound to the peripheral \(\text{Mn}^{II}\) ions (Mn2 and s.e) by four alkoxide O-atoms (O15 and s.e.) provided by two Hcht \(^2-\) ligands, which are positioned one above and one below the trimetallic chain. One protonated oxygen atom (O20 and s.e.) from the tripodal alcohol defines the JT axis of Mn1. The \(\text{Mn}^{III}_1\cdot\text{O}–\text{Mn}^{III}_1\) angle is approximately 102°, with the coordination sites of each \(\text{Mn}^{II}\) ion completed by four N-atoms from two 2,2’-bipyridine (bpy) ligands. Mn2 and s.e) are in highly distorted octahedral geometries with \(\text{cis}\) angles in the range 72.30(16)–105.65(15)° and \(\text{trans}\) angles in the range 156.0(2)–158.17(14)°. When viewed perpendicular to the \(bc\) plane, the disposition of the \([\text{Mn}_3]\) cations resembles a honeycomb-type lattice where the MeCN molecules of crystallisation are H-bonded to the terminal bonded arm of the tripodal ligand (N···O, approximately 2.8 Å), while the perchlorate anions are H-bonded to the ring of carbon atoms (O···H–C, ≥2.3 Å) and lie between the bpy groups of adjacent \([\text{Mn}_3]\) molecules. The closest intermolecular contacts between cations occur between off-set \(\pi\)-stacked bpy groups (C···C, approximately 3.5 Å).

Figure 5. (a) The molecular structure of complex 3. (b) Packing of the cations of complex 3 viewed down the \(a\)-axis. Colour code: Mn = lilac, O = red, N = blue, C = grey. H atoms, solvent molecules and counterions are omitted for clarity.

HP single crystal XRD measurements were performed in petroleum ether at \(T = 300\) K and three different pressures to a maximum of 1.25 GPa [44]. Complex 3 crystallises in the monoclinic space group \(I2/m\) and remains so in the full pressure range. Remarkably, by 0.16 GPa, there is complete elimination of the MeCN and \text{Et}_2\text{O} solvent of crystallisation. It has literally been squeezed out of
the crystal, representing the very first example of pressure-induced solvent elimination to have been observed from the crystal structure of any molecular coordination compound. This leaves large void spaces in the structure, equating to approximately 9.3% of the total volume that are gradually reduced to approximately 5.5% at 1.25 GPa. The total change in volume over the entire pressure range is approximately 10.5%, resulting in intermolecular distances shortening by approximately 0.5 Å. For example, separations between MnIII ions along the three dimensions shift from 11.919(2), 13.385(2), and 22.044(4) Å at ambient pressure to 11.331(3), 13.586(3), and 21.547(4) Å at 1.25 GPa, respectively. Despite significant changes in intermolecular interactions, there are only minor intramolecular changes. The Mn–O15 bonds contract from 1.898(3) Å at ambient pressure to 1.858(5) Å at the highest pressure, respectively. In order to address void spaces in the structure, equating to approximately 9.3% of the total volume that are gradually axially (Figure 6).

Because it exists as the 100% FR isomer, with the JT axis on Mn8 oriented equatorially rather than this, we turned our attention to [Mn12O12(O2CCH2Bu)16(H2O)4]Cl2·MeNO2 (4·CH2Cl2·MeNO2) because it exists as the 100% FR isomer, with the JT axis on Mn8 oriented equatorially rather than axially (Figure 6).

### Table 3. Comparison of the J values and the energy differences between the ground state and first/second excited spin states at ambient pressure and at 0.85 GPa for complex 3 as calculated from an isotropic fit of the susceptibility data.

| P/GPa     | S  | J/cm⁻¹  | E₁/cm⁻¹  | E₂/cm⁻¹  |
|-----------|----|---------|---------|---------|
| Ambient   | 7  | +1.15   | 4.6 (S = 6) | 9.2 (S = 5) |
| 0.85      | 7  | +0.60   | 2.4 (S = 6) | 4.8 (S = 5) |

The complex [Mn12O12(O2CCH2Bu)16(H2O)4]Cl2·MeNO2 (4·CH2Cl2·MeNO2) belongs to the prototype [Mn12O12(O2CR)16(H2O)4] family of SMMs [45,46]. The general structure of these complexes consists of a ring of eight MnIII centres surrounding a central MnIV·O4 cube, which is bridged by oxide and carboxylate ligands (Figure 6). In the case of Mn12acetate, the MnIII ions occupy two crystallographically independent sites with the eight JT axes lying in near alignment with the magnetic easy axis, affording D = −0.457(2) cm⁻¹. In combination with a S = 10 spin ground state, this leads to an effective barrier to magnetisation reversal of approximately 60 K [47]. However, bulk [Mn12] samples often contain a small percentage of a fast-relaxing (FR) JT isomer, which display a misaligned/horizontal JT axis and a much lower barrier height, $U_{\text{eff}} \approx 40$ K, and initial HP studies of the static magnetic properties of Mn12acetate at low temperatures, and HP inelastic neutron scattering (INS) measurements, had suggested some conversion of the slow relaxing (SR) isomer to the FR isomer with pressure [48–50]. However, both studies lacked any crystallographic confirmation. In order to address this, we turned our attention to [Mn12O12(O2CCH2Bu)16(H2O)4]Cl2·MeNO2 (4·CH2Cl2·MeNO2) because it exists as the 100% FR isomer, with the JT axis on Mn8 oriented equatorially rather than axially (Figure 6).
Present at ambient pressure persists. At 2.5 GPa (Figure 6), the horizontal JT bonds at Mn8 switch to vertical JT bonds, O14–Mn8–O26 (2.105(17) Å, 2.19(2) Å). Between 1.5 and 2.5 GPa, the JT bonds on the remaining Mn III sites do not change significantly. Release of pressure re-establishes the coordination seen at ambient pressure. Note that FR, H2O ligands shown in (b,c) and solvent molecules are omitted for clarity.

HP single crystal XRD measurements were performed in Daphne oil at $T = 298$ K and at three different pressures up to 2.5 GPa [51]. Complex 4 crystallises in the triclinic space group $P\overline{1}$ and remains so in the full pressure range. At ambient pressure, the formula unit contains one MeNO2 and CH2Cl2 of solvation. At 1.5 GPa, the occupancies of the solvent decreases to 0.75MeNO2 and 0.5CH2Cl2 per formula unit, and at 2.5 GPa, the solvent is removed completely—suggesting that the solvent is released into the hydrostatic medium and reabsorbed on decompression. The main structural changes within the cluster occur at the MnIII centres. At 1.5 GPa, the JT elongated bonds on Mn5, Mn6, and Mn12 become more asymmetric, while those on Mn7 and Mn9–Mn11 decrease, but only by approximately 0.02 Å on average. At Mn8, the JT bond (O208–Mn8–O25; 2.049(2) Å, 2.145(3) Å) lengths decrease, and at 1.5 GPa, the six Mn–O distances span the range 1.94(2) to 2.082(15) Å (Table 4), suggesting that the disorder present at ambient pressure persists. At 2.5 GPa (Figure 6), the horizontal JT bonds on Mn8 switch to vertical JT bonds, O14–Mn8–O26 (2.105(17) Å, 2.19(2) Å). Between 1.5 and 2.5 GPa, the JT bonds on the remaining MnIII sites do not change significantly. Release of pressure re-establishes the coordination seen at ambient pressure. Note that FR→SR isomer conversion had been previously reported to be affected by solvent loss, which is consistent with this HP crystallographic data [45,46].

Table 4. Mn–O bond lengths at Mn8 as a function of pressure. Values for significantly elongated bonds are shown in bold.

| Distance/Å | T/K | 150 | 298 | 298 | 298 |
|------------|-----|-----|-----|-----|-----|
| P/GPa      |     | 0   | 0   | 1.5 | 2.5 |
| Mn8–O108   |     | 1.893(5) | 1.930(4) | 1.98(2) | 1.88(3) | 1.932(4) |
| Mn8–O13    |     | 1.963(3) | 2.002(5) | 2.02(3) | 1.89(3) | 1.994(4) |
| Mn8–O208   |     | 2.049(2) | 1.966(4) | 1.94(2) | 1.90(3) | 1.956(4) |
| Mn8–O25    | 2.145(3) | 2.025(4) | 2.04(3) | 2.03(3) | 2.022(5) |
| Mn8–O14    | 1.961(2) | 2.012(5) | 2.082(15) | 2.105(17) | 2.015(5) |
| Mn8–O26    | 1.956(3) | 2.010(5) | 2.034(17) | 2.19(2) | 2.005(5) |
High-pressure alternating current (ac) susceptibility data (Figure 7) from ambient pressure to a maximum of 1.44 GPa was collected in Daphne oil. The ambient pressure data reveals only one peak at low temperature ($T_{\text{max}} = 2.1$ K at 1 Hz) due to the FR species. At 0.47 GPa, the low temperature peak shifts to higher temperature (approximately 2.3 K) with a significant decrease in its intensity, and a new broader peak appears at approximately 4 K, i.e., both FR and SR isomers are now present. This trend continues to higher pressures, and at 1.44 GPa, the low temperature peak disappears and only the high temperature peak is observed ($T_{\text{max}} = 4.1$ K at 1 Hz) due to the exclusive presence of the SR species. The switch is fully reversible. Arrhenius analysis of the frequency dependence affords $U_{\text{eff}}(\text{FR}) = 41$ K, $\tau_0 = 4 \times 10^{-10}$ s, increasing to $U_{\text{eff}}(\text{SR}) = 63$ K, compares well to the value, $U_{\text{eff}} = 62$ K, which was previously reported for the SR species [Mn$_{12}$O$_{12}$O$_2$(CCH$_2$Bu)$_{16}$H$_2$O)$_4$]CH$_2$Cl$_2$:MeCN. The switch from FR→SR isomer is also evidenced in the evolution of the hysteresis loop under pressure at 2 K (Figure 7), whose coercive field increases with pressure. An estimation of the axial zero-field splitting ($zfs$) from the 1.44 GPa magnetisation data affords, $D = -0.61$ K, which is in excellent agreement with that obtained from single-crystal low-temperature hysteresis loops.

The compounds [Mn$_2$O$_2$(bpy)$_4$](ClO$_4$)$_3$·3MeCN (5·3MeCN) and [Mn$_2$O$_2$(bpy)$_4$](PF$_6$)$_3$·2MeCN·H$_2$O (6·2MeCN·H$_2$O) belong to a family of mixed-valence oxo-bridged Mn$^{\text{III/IV}}$ dimers originally synthesised as models for metalloenzymes [52]. Their structures (Figure 8) contain a central [Mn$^{\text{III}}$Mn$^{\text{IV}}$O$_2$]$^{3+}$ asymmetric core with two bridging $\mu$-O$^{2-}$ ligands and two 2,2'-bipyridine (bpy) ligands completing the octahedral coordination around each Mn ion. Charge balance is maintained by the presence of three [ClO$_4$]$^-$(5·3MeCN) or three [PF$_6$]$^-$(6·2MeCN·H$_2$O) counter ions. Mn1 is in the 3+ oxidation state, with the JT axis defined by the N29–Mn1–N41 vector, which lies approximately perpendicular to the [Mn$_2$O$_2$] plane. The Mn–Mn separation and the Mn–O–Mn bridging angles are 2.7058(4) Å, 96.42(7)$^\circ$, 96.09(7)$^\circ$ in 5·3MeCN and 2.7177(7) Å, 97.00(11)$^\circ$, 96.97(11)$^\circ$ in 6·2MeCN·H$_2$O. In both cases, the solvent molecules and anions are hydrogen bonded to the protons of the bpy ligands, and the closest inter-cluster interaction is between staggered $\pi$–$\pi$ stacked bpy rings.
which increases from 2.078(5) Å at 0.18 GPa to 2.144(8) Å at 2.00 GPa. A similar change is also seen in
from 2.2221(18) Å to 2.142(6) Å. For Mn2, the changes are less significant, except for the Mn2–N5 bond,
increasing. The JT axis (N41–Mn1–N29) is significantly shortened, with the Mn1–N29 bond contracting
significant changes in the Mn1–N bond lengths, which see two of the four decreasing and one (N32)
→
5
due to the contraction of both Mn–O4 bonds (Table 5); however, for
→
2.0 GPa in
→
intramolecular changes are to the Mn–Mn distance, which contracts from 2.7058(4)
→
5
P
ff
185 cm
−
1 and complex
−
6
5·3MeCN 6·2MeCN·H2O. (b) Variations in the bond lengths from ambient pressure to 2.00 GPa in
5·3MeCN. Only statistically significant changes are shown. Colour code: Mn = lilac, O = red, N = blue, C = grey. H atoms, counterions and
solvent molecules are omitted for clarity.

HP single-crystal XRD measurements were performed in petroleum ether at room temperature [53].
Data were collected at four different pressures to a maximum pressure of 2.00 GPa for 5 and six
different pressures to a maximum pressure of 4.55 GPa for 6. Complex 5 crystallises in the triclinic
space group P-1, and complex 6 crystallises in the monoclinic space group P21/n; both remain in
the same space groups in the full pressure range. The main effect of applying pressure is the contraction
of the unit cell volume (2517.49(9) Å3; 5150.7(2) → 4207.5(6) Å3, respectively), due to the
reduction of void space and aided by the lack of any significant intermolecular interactions. The main
intramolecular changes are to the Mn–Mn distance, which contracts from 2.7058(4) Å at 2.0 GPa in 5 and from 2.7177(7) Å at 4.55 GPa in 6. In the case of 5, this change is likely
due to the contraction of both Mn–O4 bonds (Table 5); however, for 6, the variations observed for
the Mn–O distances and the Mn–O–Mn angles are not statistically significant. In 5, there are also
significant changes in the Mn1–N bond lengths, which see two of the four decreasing and one (N32)
increasing. The JT axis (N41–Mn1–N29) is significantly shortened, with the Mn1–N29 bond contracting
from 2.2221(18) Å to 2.142(6) Å. For Mn2, the changes are less significant, except for the Mn2–N5 bond,
which increases from 2.078(5) Å at 0.18 GPa to 2.144(8) Å at 2.00 GPa. A similar change is also seen in 6.

Table 5. Selected bond lengths (Å) and angles (°) for 5·3MeCN and 6·2MeCN·H2O at ambient and
maximum pressure.

|          | 5·3MeCN                        |          | 6·2MeCN·H2O                    |
|----------|--------------------------------|----------|--------------------------------|
|          | Ambient Pressure  | 2.00 GPa | Ambient Pressure  | 4.55 GPa |
| Mn1–O3   | 1.8419(15)         | 1.817(11) | 1.847(2)         | 1.828(10) |
| Mn1–O4   | 1.8621(15)         | 1.79(2)   | 1.850(2)         | 1.82(11)  |
| Mn1–N44  | 2.1093(19)         | 2.072(8)  | 2.134(3)         | 2.084(9)  |
| Mn1–N41  | 2.2053(18)         | 2.194(7)  | 2.220(3)         | 2.156(8)  |
| Mn1–N32  | 2.1666(19)         | 2.245(16) | 2.212(3)         | 2.085(9)  |
| Mn1–N29  | 2.2221(18)         | 2.142(6)  | 2.212(3)         | 2.148(8)  |
| Mn2–O3   | 1.7867(15)         | 1.79(2)   | 1.781(2)         | 1.752(12) |
| Mn2–O4   | 1.7753(15)         | 1.740(10) | 1.779(2)         | 1.791(11) |
| Mn2–N5   | 2.0971(18)         | 2.144(8)  | 2.077(3)         | 2.029(8)  |
| Mn2–N8   | 2.0160(18)         | 2.002(6)  | 2.008(3)         | 1.998(8)  |
| Mn2–N17  | 2.0813(18)         | 2.078(3)  | 2.017(9)         |            |
| Mn2–N20  | 2.0165(18)         | 2.021(5)  | 2.017(3)         | 1.982(8)  |
| Mn1–Mn2  | 2.7058(4)          | 2.676(4)  | 2.7177(7)        | 2.672(3)  |
| Mn1–O3–Mn2 | 96.42(7)      | 95.6(11)  | 97.00(11)        | 96.5(4)   |
| Mn1–O4–Mn2 | 96.09(7)      | 98.7(11)  | 96.97(11)        | 95.4(5)   |

Figure 8. (a) The molecular structure common to complexes 5·3MeCN and 6·2MeCN·H2O. (b) Variations in
the bond lengths from ambient pressure to 2.00 GPa in 5·3MeCN.
High pressure dc susceptibility data \((T = 350–20\, \text{K}, B = 0.1\, \text{T})\) were collected to a maximum pressure of \(0.87(0.84)\, \text{GPa}\) for \(5(6)\) using Daphne oil as hydrostatic medium. The behaviour of both complexes is analogous to that previously reported for \(5(6)\) across the whole temperature and pressure regime, which is consistent with the lack of any significant intramolecular structural change at low pressures. Simulations of the susceptibility data afford \(J = -177\, \text{cm}^{-1}\) and \(g = 1.96\) for \(5\) and \(J = -185\, \text{cm}^{-1}\) and \(g = 1.98\) for \(6\).

3. Cu Complexes

The choice of investigating CuII complexes was partly influenced by our initial success in MnIII chemistry where we repeatedly saw large structural changes associated with JT axes. Aligned with this was the well-known coordinative flexibility of the CuII ion, which is commonly four, five, or six coordinate, adopting a variety of geometries, and consequently, colours. Therefore, such species offered another potential variable to examine high-pressure absorption/emission spectroscopy, which would allow us to correlate changes in the metal coordination sphere to piezochromism. The Cu dimer \([\text{GuH}][\text{Cu}_2(\text{OH})(\text{cit})(\text{Gu})_2]\) \((7, H_4\text{cit} = \text{citric acid, Gu} = \text{guanidine})\) is somewhat unusual, in that it was the first reported example of a coordination compound containing neutral guanidine ligands bonded to a transition metal ion (Figure 9) [54]. At ambient pressure, complex 7 crystallises in the orthorhombic space group \(Pnma\). The two CuII ions have a distorted square pyramidal \([4 + 1]\) coordination environment. They are bridged by a \(\mu\)-OH\(^{-}\) ligand (O6), the citrate alkoxide (O1), and the citrate \(\alpha\)-carboxylate group (O4). The latter forms the long ‘axial’ bond (Cu1···O4, 2.740(4) Å). The coordination environment of each metal ion is completed by one citrate \(\beta\)-carboxylate (O2) and one neutral guanidine ligand (N1). The region of the sixth coordination site of the CuII ion is occupied by an uncoordinated \(\beta\)-carboxylate O-atom from a neighbouring molecule (Cu1···O3, 3.217(4) Å). The GuH\(^{+}\) cation is located in a pocket between the two neutral Gu ligands and is H-bonded to the anion.

![Figure 9](image)

**Figure 9.** The molecular structure of the anion in 7. Colour code: Cu = orange, O = red, N = blue, C = grey. H atoms and the counter cation are omitted for clarity.

HP single-crystal XRD measurements were performed in pentane–isopentane at room temperature at four different pressures, to a maximum of 4.23 GPa. Little intramolecular changes are seen to 1.8 GPa, but one significant intermolecular change is observed: the Cu1···O3 distance shortens by 0.264 Å to 2.953(2) Å. On increasing the pressure to 2.9 GPa, complex 7 undergoes a single-crystal-to-single-crystal phase transition to the non-centrosymmetric space group \(P2_1_2_1_2_1\) (Phase II). The Cu1···O3 contact is now defined by two independent interactions, Cu1···O30 (2.879(7) Å) and Cu2···O3 (2.610(6) Å), and the metal coordination environment changes from \([4 + 1]\) \(\rightarrow\) \([4 + 2]\) with the long contacts now defined by the intramolecular Cu···O4 bond and the intermolecular Cu1···O30 (Cu2···O3) contact. The result of these changes is the formation of a polymer via the conversion of intermolecular contacts to intramolecular bonds (Figure 10): the first example of the polymerisation of a transition metal complex with pressure. A second single-crystal-to-single-crystal phase transition occurs between 2.95 GPa and 4.23 GPa, this time to the centrosymmetric monoclinic space group \(P2_1/c\), forming Phase
III, which consists of two crystallographically independent polymeric chains. One of these chains (based on Cu1, Cu2) remains largely unchanged, while the other (based on Cu10, Cu20) undergoes significant rearrangement. Specifically, the bridging $\alpha$-carboxylate ligand twists, forcing the Cu–O–Cu moiety to be more asymmetric, the Cu10–O44 and Cu20–O44 bonds measuring 2.816(7) and 2.497(7) Å, respectively. Simultaneously, one polymer-forming bond, Cu10–O330, shortens to 2.449(6) Å, while the second (Cu20···O33, 3.098(6) Å) breaks. Thus, while the integrity of the second chain is retained, the polymerisation only involves only one Cu$^{II}$ centre, i.e., half the Cu$^{II}$ ions become [4 + 1] coordinate again.

![Figure 10](image-url)

**Figure 10.** (a) The arrangement of the molecules in Phase I at ambient pressure. (b) Formation of the polymer in Phase II at 2.95 GPa. (c,d) The two crystallographically independent polymer chains of Phase III at 4.23 GPa. Colour code: Cu = orange, O = red and N = blue. H atoms and most uncoordinated atoms are omitted for clarity.
A second, structurally related citrate/guanidine-based Cu$^{II}$ dimer, [GuH]$_4$[Cu$_2$(cit)$_2$]-2H$_2$O (8), was also studied [55]. Compound 8 (Figure 11) crystallises in the orthorhombic space group Pbca and consists of two symmetry equivalent Cu$^{II}$ ions bridged by two alkoxide O-atoms (O7 and s.e.) from the citrate ligands, the metals being further coordinated by the β-carboxylate O-atoms from each ligand (O1, O3). The four-coordinate, pseudo-tetrahedral metal centre has approximate $D_{2d}$ symmetry. In addition, each α-carboxylate group is oriented toward one of the Cu$^{II}$ centres at a Cu1–O5 distance of 2.628(3) Å, with the O5–Cu–Cu angle being 73.05(6)°. Therefore, an alternative description of the coordination sphere of the metal centre is a highly distorted [4 + 1] geometry.

![Figure 11](image1.png)

**Figure 11.** (a) The molecular structure of the anion in 8. (b) Crystal packing of complex 8 along the $a$-axis. Colour code: Cu = orange, O = red, N = blue, C = grey. H atoms and counter ions (in (a)) are omitted for clarity.

HP single-crystal XRD measurements were performed on 8 in a 1:1 mixture of pentane–isopentane to a maximum pressure of 2.20 GPa. The crystal packing of 8 consists of alternate layers of cations and anions (Figure 11b), in which the GuH$^+$ ions direct an extensive hydrogen-bonding network with the citrate ligand O-atoms and lattice H$_2$O molecules. The main effect of applying pressure is a compression along the direction of the layer-stacking in the $b$-axis (which also contains the largest voids), which decreases in length by 8.9% to 2.20 GPa (14.713(9) Å → 13.4098(7) Å). The shortening of the $a$ and $b$ axes allied to the diamond-like packing motifs formed by the guanadinium cations causes the $c$ axis to lengthen, which is an early example of negative linear compressibility in molecular solids. The most significant intramolecular change is in the Cu–O5 distance, which decreases from 2.628(3) Å at ambient pressure to 2.407(3) Å at 2.20 GPa. Therefore, the metal geometry is now 5-coordinate [4 + 1] with approximate $C_{1v}$ symmetry. Interestingly, the Cu–O5 bonds also lie along the $b$-axis, meaning that the largest intramolecular compression correlates with the largest intermolecular compression. HP single-crystal electronic spectroscopy measurements reveal that 8 undergoes a colour change from blue to green, which is due to a reduction in absorption in the 18,500–14,000 cm$^{-1}$ region. This is directly related to the reduction in the Cu–O5 bond length and the rearrangement of the Cu coordination sphere. The d–d spectrum (Figure 12) at ambient pressure consists of two bands at 15,300 and 12,800 cm$^{-1}$, which are observed in the full pressure range to a maximum of 5.5 GPa. Both bands blue shift linearly with pressure at a rate of 140 and 100 cm$^{-1}$ GPa$^{-1}$, respectively. The 15,300 cm$^{-1}$ band intensity decreases with pressure and almost disappears above 2.5 GPa. The intensity ratio in the 0–2.5 GPa range decreases in line with the reduction in the Cu–O5 distance, suggesting this to be chiefly responsible for the observed piezochromism. The main effects observed in the electronic spectra can be explained in terms of simple monomeric Cu$^{II}$ units (Figure 12b). At ambient pressure, the Cu–O5 interaction is weak, and though the Cu site symmetry is $C_1$, the spectrum can be interpreted by considering a pseudo-tetrahedral ($D_{2d}$) 4-coordinate Cu moiety, showing two allowed transitions (e → $b_2$ and $a_1$ → $b_2$). At higher pressures, the Cu–O5 interaction becomes much shorter, and the spectrum can be interpreted by considering a single allowed transition in the ($C_{4v}$) 5-coordinate Cu moiety (e → $b_2$). In short, the gradual reduction of the ‘axial’ Cu–O bond length induces a continuous transformation...
of the local Cu site symmetry from approximately \(D_{2d}\) at ambient pressure to approximately \(C_{4v}\), in which \(e \rightarrow b_2\) is the only allowed transition.

\[
\text{Figure 12. (a) Electronic absorption of complex 8 at different pressures (up to 5.5 GPa) at ambient temperature. (b) Correlation diagram showing the energy level structure of 4-coordinate Cu}^{II} \text{ from } T_d \text{ to } D_{2d}, \text{ and 5-coordinate from } D_{2d} \text{ to } C_{4v}. \text{ The arrows indicate symmetry allowed transitions.}
\]

The complexes \([\text{Cu}_2(\text{OH})_2(\text{H}_2\text{O})_2(\text{tmen})_2](\text{ClO}_4)_2\) (9, tmen = tetramethylethylenediamine), \([\text{Cu}_2(\text{OH})_2(\text{tben})_2](\text{ClO}_4)_2\) (10, tben = di-\(\text{Si}\)-butylethylenediamine), and \([\text{Cu}_2(\text{OH})_2(\text{bpy})_2](\text{BF}_4)_2\) (11, bpy = 2,2’-bipyridine) are part of a large family of hydroxo-bridged Cu\(^{II}\) dimers that have been studied since the 1970s when Hatfield and Hodgson first developed a quantitative magneto-structural correlation relating the bridging Cu\(^{II}\)–O–Cu\(^{II}\) angles in the diamond-shaped \([\text{Cu}_2(\mu-\text{OH})_2]\) core to the magnitude of the exchange interaction \([56]\). Complex 9 (Figure 13) has each Cu\(^{II}\) ion in a \([\text{CuO}_3\text{N}_2]\) square pyramidal coordination sphere, while in 10, the bulky \(\text{^tBu}\) groups of the tben ligands force the geometries of the metal ions to be intermediate between square planar and tetrahedral, with additional solvent ligation impossible, such that the Cu\(^{II}\) ions are four coordinate with \([\text{CuO}_2\text{N}_2]\) coordination spheres (Figure 14a). The Cu\(^{II}\) ions in 11 are in a JT distorted \([\text{CuO}_2\text{N}_2\text{F}_2]\) octahedral geometry, with the F–Cu–F vector defining the JT axis (Figure 14b). The Cu–O–Cu angles are 102.03(13)° in 9, 102.72(6)° and 101.62(6)° in 10, and 97.40(14)° in 11. At ambient pressure, they crystallise in the monoclinic space groups \(P2_1/c\) (9), \(C2/c\) (10), and \(C2/m\) (11).

\[
\text{Figure 13. The molecular structure of complex 9 at (a) 0.25 GPa and (b) 2.5 GPa. Colour code: Cu = orange, O = red, N = blue, C = grey, Cl = green. H atoms (and counterions in (a)) are omitted for clarity.}
\]
HP single-crystal XRD measurements were performed using petroleum ether as hydrostatic medium [57]. Data were collected at 0.25, 0.70, 1.20, and 2.50 GPa for 9, at 0.21 and 0.90 GPa for 10, and at 0.30, 0.80, 1.53, 2.25, 2.80, 3.50, 4.00, 4.30, and 4.70 GPa for 11. Crystals of 10 and 11 remain in the same space group in the full pressure range, whereas complex 9 undergoes a phase transition between 1.20 and 2.50 GPa from monoclinic $P2_1/c$ to triclinic $P$-1. In all cases, the primary effect of applying pressure is a reduction of the unit cell, the compressions being assigned to the removal of void space due to the absence of any significant intermolecular interactions. The secondary effect is intramolecular. In 9, the Cu–O–Cu angle becomes smaller, from 102.03(13)$^\circ$ to 99.7(7)$^\circ$ at 1.20 GPa, with a concomitant shortening of the Cu–Cu distance from 2.9784(12) Å to 2.939(3) Å (Table 6). At ambient pressure, one H$_2$O molecule is bonded to each Cu$^{II}$ ion, which is approximately perpendicular to the Cu$_2$O$_2$ plane (Cu–Cu–O = 91.41(16)$^\circ$; Figure 13), but it becomes severely distorted at higher pressures (Cu–Cu–O = 80.4(7)$^\circ$). The reason for this bending appears to be the shortening of the intermolecular O(ClO$_4$)···O(H$_2$O) distance to just 3.50 Å. Further increases in pressure lead to a phase transition from the monoclinic space group $P2_1/c$ to the triclinic space group $P$-1 between 1.20 and 2.50 GPa, with the asymmetric unit now containing two full dimers and four perchlorate anions. The loss of symmetry is caused by the elimination of one H$_2$O molecule from half the dimers, producing two different complexes: one with two H$_2$O molecules (one bonded to Cu1 and Cu1*) and one with only one H$_2$O molecule (bonded to Cu3; Figure 13). This was the first reported example of pressure-induced H$_2$O elimination. In both dimers, the decreasing Cu–Cu distance with increasing pressure continues, reaching 2.914(3) Å for Cu1–Cu1* and 2.849(9) Å for Cu3–Cu4 at the highest pressure (2.5 GPa) measured.

Complexes 10 and 11 are less affected by the application of pressure. In 10, the Cu–Cu distance decreases from 2.9784(3) Å at ambient pressure to 2.908(7) Å at 0.90 GPa, with the Cu–O–Cu angles changing from 102.76(6)$^\circ$ and 101.62(6)$^\circ$ to 99.3(10)$^\circ$ and 104.2(11)$^\circ$. The shortening of the Cu–Cu distance is likely due to the contraction of the bond between Cu2 and the two bridging hydroxide ions decreasing from 1.9198(12) Å to 1.77(3) Å, thus becoming one of the shortest Cu$^{II}$–OH distances ever reported. The presence of the two BF$_4$$^-$ anions in 11 results in a more rigid structure, reducing the effect of applying pressure. The Cu–F distances decrease from 2.775(2) Å to 2.503(3) Å (ambient pressure → 4.7 GPa), the Cu–Cu distance changes from 2.8663(17) Å to 2.8210(19) Å, and the Cu–O–Cu angles decrease from 97.40(14)$^\circ$ at ambient pressure to 95.6(2)$^\circ$ at 4.7 GPa.

Figure 14. (a) The molecular structure of complex 10 at ambient pressure. (b) The molecular structure of complex 11 at ambient pressure. Colour code: Cu = orange, O = red, N = blue, C = grey, B = pink, F = pale green. H atoms (and counterions in (a)) are omitted for clarity.
Table 6. Selected distances (Å) and angles (°) in compounds 9–11 as a function of pressure (GPa).

| P/GPa | 9                  | 10               | 11              |
|-------|--------------------|------------------|-----------------|
|       | Cu1--Cu1*         | Cu1--O10--Cu1*   | Cu1--O10--Cu1*  |
| ambient| 2.9784(12)        | 102.03(13)       | 91.41(16)       |
| 0.25  | 2.9578(19)        | 101.2(3)         | 88.7(3)         |
| 0.70  | 2.946(2)          | 101.1(3)         | 87.4(3)         |
| 1.20  | 2.939(3)          | 99.7(7)          | 80.4(7)         |

|       | Cu1--Cu2          | Cu1--O1--Cu2     | Cu1--O2--Cu2    |
|-------|-------------------|------------------|-----------------|
| 2.50  | 2.914(3)          | 98.4(4)          | 99.5(6)         |
| 2.50  | 2.004(16)         | 93.9(13)         | 94.0(7)         |

|       | Cu1--Cu1*         | Cu1--O1--Cu1     | Cu1--O2--Cu1    |
|-------|-------------------|------------------|-----------------|
| ambient| 2.8663(17)        | 1.908(2)         | 2.775(2)        |
| 0.30  | 2.8689(17)        | 1.910(2)         | 2.768(3)        |
| 0.80  | 2.8649(14)        | 1.911(2)         | 2.711(2)        |
| 1.53  | 2.8544(12)        | 1.9069(19)       | 2.655(2)        |
| 2.25  | 2.8427(15)        | 1.908(2)         | 2.609(3)        |
| 2.80  | 2.8422(12)        | 1.907(2)         | 2.577(2)        |
| 3.50  | 2.8331(13)        | 1.914(2)         | 2.548(2)        |
| 4.00  | 2.8313(14)        | 1.913(3)         | 2.530(3)        |
| 4.30  | 2.8374(17)        | 1.920(3)         | 2.543(4)        |
| 4.70  | 2.8210(19)        | 1.904(3)         | 2.503(3)        |

HP dc magnetic susceptibility data ($T = 350–20$ K, $B = 0.1$ T) were collected at ambient pressure to a maximum pressure of 0.84 GPa (9), 0.87 GPa (10), and 0.86 GPa (11) using Daphne oil. Simulation of the susceptibility data at ambient pressure reveals strong antiferromagnetic exchange in 9 and 10 ($J = -260$ cm$^{-1}$ and $J = -252$ cm$^{-1}$, respectively) and moderate ferromagnetic exchange in 11 ($J = +22$ cm$^{-1}$). The $\chi_m T$ value for complexes 9 and 10 at low temperatures (up to 90 K) are 0 cm$^3$ mol$^{-1}$ at all pressures. As the temperature increases, the $\chi_m T$ value of 9 increases, following different paths as a function of the applied pressure, reaching a maximum value of 0.28 cm$^3$ mol$^{-1}$ K at ambient pressure and 0.39 cm$^3$ mol$^{-1}$ K at 0.84 GPa. The data follow a similar trend for complex 10 with $\chi_m T$ changing from 0.30 cm$^3$ mol$^{-1}$ K to 0.34 cm$^3$ mol$^{-1}$ K (ambient pressure → 0.87 GPa) at $T = 350$ K. This behaviour reveals a weakening of the antiferromagnetic interaction between the Cu$^{II}$ ions. The parameters obtained from the simulations at different pressures (Table 7) show that $J$ decreases from $-260$ cm$^{-1}$ to $-203$ cm$^{-1}$ for 9 and from $-252$ cm$^{-1}$ to $-228$ cm$^{-1}$ for 10 with increasing pressure, which is in agreement with magneto-structural correlations developed for [Cu$_2$(OH)$_2$] dimers in which decreasing Cu–O–Cu angles, Cu–O, and Cu–Cu distances are all expected to decrease $|J|$ [58]. HP susceptibility measurements of 11 show a small increase in the $\chi_m T$ value with increasing pressure, with $J$ increasing from +22.0 cm$^{-1}$ at ambient pressure to +29.4 cm$^{-1}$ at 0.86 GPa.
Previous HP powder XRD (PXRD) and magnetic susceptibility measurements on the coordination polymer [Cu^{II}F_{2}(H_{2}O)_{2}(pyz)] (12, pyz = pyrazine) had shown successive structural phase transitions and a pronounced change in the effective dimensionality of the extended Cu^{II}..Cu^{II} exchange interactions from 2D to 1D [59]. To further complement this study, we performed detailed HP single-crystal XRD and HP single-crystal electron paramagnetic resonance (EPR) spectroscopy on 12 in order to provide direct information regarding any pressure-induced reorientation of the JT (d_{xz}−d_{yz}) orbitals. At ambient pressure, complex 12 crystallises in the monoclinic space group P2_{1}/c with one Cu^{II} ion in the asymmetric unit (Figure 15). The six-coordinate, JT distorted octahedral Cu^{II} ion is bonded to two O-atoms (1.984(4) Å) from the two H_{2}O ligands, two F− ions (1.908(4) Å), and two N-atoms (2.454(6) Å) from the pyz ligands. The latter define the orientation of the JT axis, whereby the pyz ligands direct the formation of 1D chains along the a-axis of the unit cell. In the bc plane, these chains are linked into a 2D network by short Cu−OH···F−Cu H-bonds (2.623(4) Å and 2.607(4) Å). Therefore, the magnetic d_{xz−y^2} orbital of the Cu^{II} ion lies in the CuF_{2}O_{2} (bc) plane, as confirmed by ambient low temperature magnetisation data, which show a 2D antiferromagnetic magnetic order with T_{N} = 2.54 K.

| 9     | 10     | 11    |
|------|--------|-------|
| P (GPa) | J (cm\(^{-1}\)) | P (GPa) | J (cm\(^{-1}\)) | P (GPa) | J (cm\(^{-1}\)) |
| ambient | −260 | ambient | −252 | ambient | +22 |
| 0.22 | −222 | 0.30 | −246 | 0.40 | +24 |
| 0.59 | −220 | 0.58 | −234 | 0.61 | +25.5 |
| 0.84 | −203 | 0.87 | −228 | 0.86 | +29.4 |

Table 7. Comparison of the J values as a function of pressure for complexes 9−11, with g = 2.09 for 9 and 10, and g = 2.11 for 11.

Figure 15. The molecular structure of complex 12 showing (a) the 2D network in the bc-plane, and (b) the 1D chains directed by the pyz ligands along the a-axis. The dashed light blue lines highlight the Cu−OH···F−Cu H-bonds. Colour code: Cu = orange, O = red, N = blue, C = grey, F = yellow, H = pale green.

HP single-crystal XRD measurements were performed in petroleum ether, with room temperature data collected at 0.50, 0.90, 1.20, 1.80, 2.20, 2.50, 2.85, and 3.30 GPa [60]. The initial effect of pressure is a compression of the unit cell, and while the Cu−N, F, and O distances do not change significantly up to 1.2 GPa; both Cu−OH···F−Cu hydrogen bonds compress to 2.515(13) Å. This value is exceptionally short for this type of interaction and hints at a build-up of strain in the bc plane. At 1.8 GPa, the phase modification (Phase II) observed in the PXRD measurements occurs. The crystallographic symmetry is maintained, but the Cu−N bond lengths decrease by approximately 0.4 Å to 2.039(3) Å, and the Cu−O bonds increase by 0.3 Å to 2.316(3) Å. This reflects the reorientation of the JT axis from the N−Cu−N direction to the O−Cu−O direction, and it means the magnetic d_{xz−y^2} orbital is now oriented
along the 1D pyrazine chains. This structural reorganisation simultaneously relieves the tension in the OH···F hydrogen bonds, which increase to 2.702(3) and 2.626(3) Å, respectively. 12 undergoes a second, even more disruptive, pressure-induced phase transition between 2.85 and 3.30 GPa to the triclinic space group P-1 (Phase IV). During this transition, one H2O molecule per Cu unit from two-thirds of the chains is lost, forcing a dimerisation of the chains through the F⁻ ions (Figure 16). The remaining one-third of the chains are unchanged. Interestingly, and in contrast to 3 where the solvent was ejected from the lattice, the expelled water molecules remain in the crystal lattice and sit between the monomeric and dimeric chains, which are held in place by the OH···F H-bonding network. In Phase IV, the JT axes are now oriented along the O–Cu–F bonds (Cu2-O1, 2.22(3) Å, Cu2-F6*, 2.28(2) Å), and adjacent Cu ions within the dimerised chains are now bridged directly by F⁻ ions (Cu2–F6, 1.908(18) Å; Cu2–F6–Cu2*, 103.0(8)°). A separate study has revealed a third transformation route at 3.3 GPa which leads to a phase in which the chemical connectivity and orientation of the JT axes in Phase II were retained but its symmetry is reduced to triclinic, and the orientation of the pyrazine ligands changes [61].

**Figure 16.** Phases I, II, and IV observed in the HP single-crystal XRD for complex 12. The green bonds highlight the orientation of JT axis (d\(\tau\)) of the Cu\(^{II}\) ion along the a-axis of the cell. The magnetic d\(\tau\), orbital lies perpendicular to this, in the bc plane. Phase III observed in the pXRD measurements [59] was not seen in the single-crystal XRD measurements. Colour code is the same as in Figure 15. H atoms are omitted for clarity.

HP single-crystal EPR measurements at 0.67 GPa (Figure 17) as a function of field orientation at 69.3 GHz and 10 K show a single, sharp peak with strong angle dependence and \(g\)-value extrema of \(g_\parallel = 2.42\) and \(g_\perp = 2.08\). The former corresponds to the direction parallel to the JT axis. At 1.82 GPa and 65.7 GHz two signals are observed, one with a similar angle dependence to the low-pressure signal and a second with a weaker angle dependence and \(g\)-values in the 2.05–2.10 range. This corresponds to field rotation within the plane of the d\(\tau\), orbital, i.e., the \(\perp\) orientation. Measurements at 96 GHz (Figure 17b) also suggest that part of the sample has transformed to Phase II, i.e., the mechanism of the phase transformation occurs in domains rather than via a concerted transition over the whole crystal; this is local information only visible through spectroscopy and not recognised from the crystallographic data, which yields only an average structure. The strongly angle-dependent signal vanishes completely upon increasing the pressure to 2.1 GPa, and the EPR intensity is observed only in a single, broad low \(g\)-value signal that displays weak angle dependence. This is direct evidence that the magnetic d\(\tau\) orbital has switched from the CuF\(_2\)O\(_2\) plane to the CuF\(_2\)N\(_2\) plane. Access to the pressure at
which the second phase transition was observed (i.e., to Phase IV) was beyond the technological capabilities of the plastic EPR cells.

Figure 17. (a) Experimental electron paramagnetic resonance (EPR) spectra recorded at 10 K as a function of field orientation within the ab plane of a single crystal (transmission offset). The three panels correspond to three different pressures and microwave frequencies. Spectra were recorded every 10°, with 0° corresponding to the field along the a-axis; the field orientations corresponding to the top and bottom traces are indicated in each panel. (b) EPR peak positions taken from (a) together with data obtained at other frequencies (not shown), which are plotted as their corresponding g-factors versus the orientation of the applied field within the ab plane of the crystal.

4. Ni Compounds

Research in the field of Single-Ion Magnets (SIMs) has focussed on achieving precise control over the coordination geometry of a single paramagnetic (d-/f-block) metal ion in order to construct a specific ligand field that generates first order spin-orbit coupling (SOC) [62–64]. An attractive option for HP measurements is Ni11, for which a range of 4-/5-coordinate, air-/moisture-stable species are known. For example, ambient pressure magnetic measurements and HF-EPR studies performed on both oriented single crystals and powder samples of the complex [Ni(MeDABCO)2Cl2](ClO4) (13, MeDABCO = 1-methyl-4-aza-1-azoniabicyclo[2.2.2]octanium) had shown it to possess |D| ≥ 400 cm⁻¹ [65]. Given that |D| is highly sensitive to changes in coordination geometry, it appeared to be an ideal candidate to explore the effects of pressure. Complex 13 (Figure 18) crystallises in the orthorhombic space group Pca21. The structure describes a simple 5-coordinate, slightly distorted trigonal prismatic Ni11 ion bonded to two axial MeDABCO + ligands and three equatorial Cl⁻ ions (Table 8). The structural distortions away from ideal D3h symmetry arise from the JT effect, which splits the degeneracy of the dₓz−dᵧz and dₓ²−y²−dₓy pairs of orbitals [66].

Table 8. Selected distances (Å) and angles (°) in compound 13 as a function of pressure (GPa).

| P/GPa | Ni1–N11 | Ni1–N21 | Ni1–Cl1 | Ni1–Cl2 | Ni1–Cl3 |
|-------|---------|---------|---------|---------|---------|
| ambient | 2.230(2) | 2.199(6) | 2.190(6) | 2.190(6) | 2.190(6) |
| 1.65 | 2.215(2) | 2.295(2) | 2.3016(9) | 2.3016(9) | 2.3016(9) |
| | Ni1–N11 | Cl1–Ni1–Cl2 | Cl2–Ni1–Cl3 | Cl1–Ni1–Cl3 |
| ambient | 177.1(1) | 123.2(1) | 119.0(1) | 117.7(1) |
| 1.65 | 176.2(2) | 124.3(1) | 123.4(1) | 112.3(1) |
1.08 GPa show clear agreement with a decrease in which contribute 
Å (Table 9). At ambient pressure, the computed pressures, to a maximum of 1.65 GPa; unit cell parameters were determined over the pressure range 0 GPa to 1936.4(3) Å

B = 1 T) collected at four different pressure points to a maximum pressure of 1.08 GPa show clear agreement with a decrease in |D| and an increase in |E| with pressure (Table 10). The availability of theoretical methods for the calculation of anisotropy, exchange coupling, and other magnetic parameters, together with elucidation of the orbital interactions that influence them, is a major development in the field of high-pressure coordination chemistry. We anticipate that it will not only enable meaningful conclusions to be drawn from data which can on occasion suffer from

In contrast, there are significant changes to the equatorial bond angles: Cl1–Ni1–Cl2 and Cl2–Ni1–Cl3 increase to 124.3(1)° and 123.4(1)°, respectively, while Cl1–Ni1–Cl3 decreases to 112.3(1)°. A small decrease in the trans N–Ni–N angle is also observed (177.1(1)°→176.2(2)°). The net result is a further lowering of the symmetry around the metal centre, as confirmed by continuous shape measures, which reveal $S(D_{3h}) = 0.09$ at ambient pressure and $S(D_{3h}) = 0.23$ at 1.65 GPa [68].

Ab initio calculations performed on the four structures collected at 0.58, 0.90, 1.40, and 1.65 GPa were employed to extract the zfs parameters ($D$, $E$) associated with the gradual loss of symmetry (Table 9). At ambient pressure, the computed $D_{zz}$ axis is found to lie along the pseudo-C3 axis (the N–Ni–N direction), and the computed $g_{zz}$ is found to coincide with this axis. The origin of the very large $D$ value is the closely lying $d_{z^2−r^2}$ and $d_{xy}$ orbitals (their separation is approximately 239 cm$^{-1}$), which contribute $−488$ cm$^{-1}$ to the total $D$ parameter. Significant, but smaller, positive contributions stem from excitations from the $d_{xz}$ and $d_{yz}$ orbitals to the $d_{xy}$ orbital. Calculations on the structure collected at higher pressure suggest a decrease in $D$ by approximately one-third, from $−399$ cm$^{-1}$ at 0 GPa to $−264$ cm$^{-1}$ at 1.4 GPa, highlighting the extreme sensitivity of the magnetic anisotropy to small structural changes in the Cl–Ni–Cl angles (Table 9). Specifically, these changes lead to a larger separation between the $d_{xy}$ and $d_{z^2−r^2}$ orbitals, which directly correlates with a decrease in the major contribution to $|D|$. This is accompanied by an increase in the rhombic anisotropy, $|E|$, from 0.10 cm$^{-1}$ at ambient pressure to 0.86 cm$^{-1}$ at 1.4 GPa, which originates from the increased separation between the and $d_{yz}$ orbitals and an increase in the tunnel splitting between the $M_S = ±1$ states. Using the ab initio calculations and HF-EPR data as a starting point, simulations of HP dc magnetic susceptibility data ($T = 290−2$ K, $B = 1$ T) collected at four different pressure points to a maximum pressure of 1.08 GPa show clear agreement with a decrease in $|D|$ and an increase in $|E|$ with pressure (Table 10).
poor statistics, but, as this and the next study show, it also pinpoints the electronic source of the magneto-structural correlations seen experimentally.

Table 9. NEVPT2 calculated $D$ and $E$ values computed from the high-pressure single-crystal X-ray data along with the most prominent contribution to $D$, the tunnel splitting of the $M_S = \pm 1$ levels, and the $\delta$ value computed for the structure.

| $P$/GPa | $D$/cm$^{-1}$ | $E$/cm$^{-1}$ | Contribution from 1st Excited State (NEVPT2)/cm$^{-1}$ | Tunnel Splitting/cm$^{-1}$ | Sum of Cl–Ni–Cl Angle Deviation, $\delta^\circ$ |
|---------|-------------|-------------|-------------------------------------------------|-------------------|---------------------------------|
| ambient | $-399$     | 0.104       | $-488$                                            | 0.21              | 6.49                            |
| 0.58    | $-347$     | 0.208       | $-435$                                            | 0.42              | 7.64                            |
| 0.90    | $-317$     | 0.419       | $-403$                                            | 0.84              | 10.44                           |
| 1.40    | $-264$     | 0.861       | $-346$                                            | 1.72              | 15.19                           |
| 1.65    | $-264$     | 0.871       | $-346$                                            | 1.75              | 15.4                            |

Table 10. Parameters used for the simulation of the magnetic data for complex 13.

| $P$/GPa | $g_z$   | $g_x$ | $g_y$ | $D$/cm$^{-1}$ | $E$/cm$^{-1}$ |
|---------|--------|-------|-------|---------------|---------------|
| ambient | 3.36   | 2.05  | 2.05  | $-399$        | 0.10          |
| 0.52    | 3.28   | 2.12  | 2.13  | $-349$        | 0.22          |
| 0.79    | 3.24   | 2.16  | 2.18  | $-323$        | 0.33          |
| 1.08    | 3.20   | 2.20  | 2.22  | $-295$        | 0.52          |

5. Re Compounds

Our interest in single ions possessing large magneto-anisotropies next led to Re$^{IV}$ [69]. The complexes [ReCl$_4$(MeCN)$_2$]MeCN (14) and [ReBr$_4$(bpym)] (15, bpym = 2,2’-bipyrimidine) (Figure 19) are characterised by large magnetic anisotropies and significant intermolecular magnetic exchange interactions mediated through Re–X···X–Re type contacts (X = halogen), resulting in spin canting (the non-collinearity of neighbouring spin centres) and magnetic order at low temperature ($T_C$ (14) = 6.5 K, $T_C$ (15) = 18.0 K) [70,71]. The dipolar exchange pathways arise as a result of the spin density from the Re$^{IV}$ ion being significantly delocalised onto the peripheral atoms of the ligand. Intermolecular magnetic exchange interactions can be modified by changing intermolecular distances, i.e., making these distances shorter would be expected to increase the strength of the exchange and increase the ordering temperature, and one way of achieving this is to exert hydrostatic pressure.

![Figure 19](image-url) Figure 19. (a) The molecular structure of (a) 14 and (b) 15. Colour code: Re = purple, N = blue, C = grey, Cl = green, Br = light brown. H atoms and solvent molecules are omitted for clarity.

Compounds 14 (Pnma) and 15 (P2$_1$/c) crystallise in orthorhombic space groups, with the metal ion occupying a distorted octahedral environment, bonded to two N-atoms and four halides. The extended structures display staggered zig-zag chains that propagate along the $a$-axis of the unit cell via interhalide dispersive interactions (Figure 20). Under pressures of up to 4.30 GPa, unit cell...
volumes decrease by 20% (14) and 14% (15), the principal component of compression occurring down the c-axis of the unit cell in both cases [72]. Complex 15 undergoes a phase transition between 1.93 and 3.06 GPa to a monoclinic phase with space group \(P2_1\), and when subjected to complete compression–decompression cycles to 4 GPa, both complexes return to their original ambient pressure unit cell/space group. In addition, ambient pressure crystal structures solved at \(T = 4\) K show that both species retain their room temperature structures. The most significant structural changes observed under pressure in 14 and 15 occur in the intermolecular Re–X···X–Re distances. For compound 14, the Re–Cl4···Cl2–Re distance shortens by approximately 0.6 Å to 3.362(11) Å, while for compound 15, the Re-Br2···Br4-Re distance decreases by 0.31 Å to 3.5718(2) Å.

High-pressure SQUID magnetometry was performed on microcrystalline samples of 14 and 15 using Daphne oil as the hydrostatic medium. HP dc magnetic measurements (\(T = 50.0–2.0\) K, \(B = 0.01\) T) were collected at ambient pressure to a maximum pressure of 4.1 GPa for 14 (4.2 GPa for 15). These experiments show that the application of hydrostatic pressure leads to an increase in ordering temperature (Figure 21). At the highest pressures measured, \(T_C\) (determined from field cooled and zero-field cooled measurements as a function of temperature) reaches 28 K at 4.10 GPa for 14, and 42 K at 4.30 GPa for 15. For 14, this represents a four-fold enhancement, with the rate at which \(T_C\) increases being 5.1 and 5.4 K GPa\(^{-1}\) for 14 and 15, respectively. The phase transition observed for compound 15 does not affect the monotonic increase of the ordering temperature, and in both cases, the changes in \(T_C\) are reversible; recovery of the ambient pressure \(T_C\) is observed when the pressure is released from the cell.

Figure 20. The extended structures of (a) 14 and (b) 15. Colour code: Re = purple, N = blue, C = grey, Cl = green, Br = light brown. H atoms and solvent molecules are omitted for clarity. The dashed lines show the halide–halide interactions.

Figure 21. Pressure dependence of the ordering temperature of (a) compound 14 and (b) compound 15.
Density functional calculations show that the shortest Re-X···X-Re pathways generate the most efficient magnetic exchange interactions at all pressures, and that an increase in the magnitude of J in 14 and 15 is observed when external pressure is applied, which is in agreement with increasing $T_C$ in both systems. The correlation between parameters is simple; the external applied pressure produces a linear increase in J and a linear increase in $T_C$ (Figure 22).

![Figure 22](image_url)  
**Figure 22.** Magneto-structural correlations in 15. The blue circles represent the pressure dependence of the ordering temperature, while the red circles represent the exchange interaction J. The lines represent the linear best-fit.

6. Conclusions

Despite HP single-crystal XRD being available since the 1950s, reports of its combination with other HP techniques (magnetometry, INS, EPR, absorption/emission/Raman spectroscopy) to examine magneto-structural relationships in molecule-based magnets remain rather rare. This is surprising given the enormous potential benefits on offer. This may be partly due to technology—the design and manufacture of pressure cells for other types of measurements (e.g., magnetometry, EPR) lag behind that of DACs for single-crystal XRD, and these pressure cells often do not reach the same high pressures. Sod’s law dictates this is often where the structural changes occur. However, this is not always the case, and as we have summarised above, it is possible to extract a wealth of fascinating and useful information. Looking just at magnetic coordination compounds, we have discovered that pressure can lead to significant changes in bond angles and distances around metal centres, reorientation of JT axes, the breaking and forming of bonds, polymerisation/depolymerisation, multiple phase transitions that can depend on the hydrostatic medium, colour changes, switching of the sign of magnetic exchange interactions (F↔AF), and enormous changes in zero-field splitting parameters and magnetic ordering temperatures. This is far more than we had first anticipated, and it clearly goes well beyond the removal of voids. This wealth of intramolecular effects distinguishes coordination complexes from purely organic materials, where, except for leading to changes in conformation, the effects of pressure are usually exclusively intermolecular, albeit with some notable exceptions [73]. While it is currently not possible to predict what distortion will occur *a priori*, it is clear that intermolecular effects are extremely important in determining the sensitivity to pressure of individual bond lengths, angles, and torsions. For example, in a related study on the (non-magnetic) Ni complexes of 6-fluoro and 6-methoxy salicylaldoxime, the Ni–O bonds were more sensitive to pressure in the former, and the Ni–N bonds were more sensitive in the latter [74]. The effect could be traced to the distribution of interstitial voids formed between the complexes, the less sensitive bonds being oriented toward the voids. In the Mn$_{12}$ acetate derivative discussed in Section 2, the directions of greatest linear strain lay in the direction of the isomeric Jahn–Teller axis, so that its reorientation can be similarly viewed as being driven by the local intermolecular structure distortion. More research into the role played by intermolecular interactions in the intramolecular pressure response of these materials would be...
very welcome. More generally, high-pressure work requires high quality, mechanically robust crystals. The body of a diamond anvil cell limits the volume of the reciprocal space that can be sampled, and so high symmetry is an advantage. The same effect tends to limit the complexity of refinement models, and so the absence of disorder and relatively low thermal motion are also highly desirable. With ever-improving cell design now making a breadth of characterisation techniques available to HP studies, we hope that this review article highlighting our own work can serve as an example, and as a stimulus, for other researchers to realise that HP techniques may be a valuable addition to their experimental toolkit. One area that we feel will benefit in the short term from combined HP studies is the understanding of the magnetisation relaxation dynamics of SIMs. The latter depend on symmetry, coordination geometry, crystal field, ligand donor strength, and crystal packing. All of these factors are sensitive to pressure, and even small changes to metal geometries can have a profound effect on magnetic anisotropy. Thus, HP structural studies in combination with HP magnetometry, INS, EPR, Raman spectroscopy, and electronic spectroscopy would provide detailed insight into the mechanisms of the relaxation behaviour, including the role of optical and acoustic phonons.

Author Contributions: A.E.-B., S.A.M., M.M. and E.K.B. wrote the manuscript. S.P., K.V.K. and M.R.P. proof-read, reviewed and edited the manuscript. All authors have read and agreed to the published version of the manuscript.

Funding: This research received funding from the EPSRC, grant numbers EP/D503744/1, EP/D503752/1, EP/E06471X/1, EP/H004106/1, EP/K033646/1, EP/K033662/1, EP/K033549/1, EP/N01351X/1. A.E.B. thanks ANID (Chile) for a Postdoctoral Fellowship, grant number 74190043. The work has also benefited from access to beamtime, initially at the Synchrotron Radiation Source, Daresbury Laboratory, and lately at Diamond Light Source. We are grateful to instrument scientists Simon Teat, John Warren, David Allan and Mark Warren for their extensive help during beamtime.

Acknowledgments: We would like to acknowledge the hard work and dedication of all the PhD students and PDRAs who have worked on these projects, funded on the above-named grants. Alessandro Prescimone, Pascal Parois, Scott McKellar, Javier Sanchez-Benitez, Kyle Galloway, Sergio Sanz, Xiao Wang, Chris Woodall, Jose Martinez-Lillo, Charlie McMonagle, Gavin Craig, Helen Duncan, Angelos Canaj and Marco Coletta.

Conflicts of Interest: The authors declare no conflict of interest.

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