# An Air Stable, Radical-Bridged, Dinuclear Dysprosium Single Molecule Magnet and Its Neutral Counterpart: Redox Switching of Magnetic Relaxation Dynamics

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Supporting Information

# Contents

## Experimental

### Synthesis

*General*

All manipulations were carried out under an inert atmosphere of Ar or $N_2$ unless otherwise noted. Dy(tmhd)$_3$ was purchased from Alfa Aesar, dried under vacuum at 100° C and stored in the glovebox prior to use. $Cp_2Co$ was purchased from Beantown Chemical and stored under an inert atmosphere prior to use. Toluene was purchased from Sigma Aldrich, sparged with $N_2$, purified using an MBRAUN solvent purification system, and stored over molecular sieves under an inert atmosphere prior to use. Anhydrous pentane was purchased from Sigma Aldrich and stored over molecular sieves under an inert atmosphere prior to use. bptz was synthesized according to a literature procedure. Infrared spectra were obtained using a Nicolet Nexus 470 FT-IR Spectrometer. Elemental analyses were performed by Atlantic Microlabs, Inc., Norcross, GA.

*Synthesis of [Dy(tmhd)$_3$]$_2$(bptz)* (**1**)

A vial was charged with 140.5 mg Dy(tmhd)$_3$ (0.1972 mmol). A second vial was charged with 23.2 mg bptz (0.0982 mmol). The compounds were both dissolved in 10 mL dichloromethane (DCM) and mixed. Upon mixing, the reaction becomes a vibrant red-orange color. The reaction stirred overnight. Afterwards, the solvent was removed under vacuum, and the crude material was extracted using 10 mL pentane. The extract was filtered, and the solution was stored in the freezer, yielding red crystals of **1**. Yield: 34.8 mg (21.3 %). X-ray quality crystals were grown from a hexane solution of **1** at -30° C. IR (nujol mull, cm$^{-1}$) 1606 (w), 1590 (m), 1577 (s), 1530 (m), 1506 (s), 1491 (w), 1423 (vs), 1395 (m), 1359 (m), 1246 (vw), 1227 (w), 1179 (w), 1141 (w), 1072 (vw), 1009 (vw), 933 (vw), 870 (m), 792 (m), 760 (w). Elem. Anal. Calcd. for $C_{78}H_{122}Dy_2N_6O_{12}$ (**1**): C 56.41%, H 7.41%, N 5.06%; Found: C 56.91%, H 7.47%, N 5.30%.

*Synthesis of {Cp$_2$Co}{[Dy(tmhd)$_3$]$_2$(bptz)}* (**2**)

A vial was charged with 159.8 mg Dy(tmhd)$_3$ (0.224 mmol). A second vial was charged with 26.2 mg bptz (0.111 mmol). A third vial was charged with 21.2 mg $Cp_2Co$ (0.112 mmol). The $Cp_2Co$ was dissolved in 10 mL toluene and added to the bptz. The mixture was stirred for 10 minutes and then added to the Dy(tmhd)$_3$. Upon addition to the Dy(tmhd)$_3$, the reaction turned a deep blood red color, and it was allowed to stir at room temperature overnight. In the morning, the solvent was removed under vacuum. Then, the residue was extracted with pentane and filtered. X-ray quality crystals of **2** grew from the pentane extract at room temperature overnight. Yield: 38.3 mg (18.7 %). IR (nujol mull, cm$^{-1}$) 3084 (vw), 1588 (vs), 1576 (vs), 1535 (s), 1504 (vs), 1456 (vs), 1434 (vs), 1358 (s), 1276 (w), 1243 (w), 1227 (m), 1177 (m), 1139 (m), 1104 (vw), 1073 (vw), 1047 (w), 1011 (w), 961 (vw), 867 (m), 790 (m), 751 (m), 736 (w), 723 (w), 640 (w), 602 (w), 476 (m). Elem. Anal. Calcd. for $C_{98}H_{156}CoDy_2N_6O_{12}$ (**2**): C 57.13%, H 7.19%, N 4.54%; Found: C 57.47%, H 7.30%, N 4.07%.

**X-ray Crystallography**

Suitable crystals of **1** and **2** were selected from the mother liquor and placed under paratone oil under ambient conditions. The crystals were mounted on a 100 µm MiTeGen microloop and placed in a cold stream of $N_2$ at 110 K. The crystals were diffracted with either an IµS Mo microsource (λ = 0.71073 Å) or a Mo sealed tube source (λ = 0.71073 Å). An initial unit cell was determined by three ω scans consisting of 0.5° frames and a sweep width of 15° (**2**) or 6° (**1**) with exposure times of 5 – 20 seconds. Final unit cell constants were determined by refinement of cell parameters against reflections obtained from the full data collection. A full data collection strategy was determined using the QUEEN plugin of APEX3.[1] A full data set for each structure was collected to a resolution of at least 0.82 Å. Full details of the data collections are presented in Table S1 and the refinement details for each compound are detailed below.

The structures were solved using the intrinsic phasing routine of SHELXT. [2] Non-hydrogen atoms were located from the difference Fourier electron density map and refined using SHELXL-2014 using

OLEX2 as a graphical user interface. [3] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed at calculated positions and their thermal parameters were allowed to ride on the thermal parameters of their host atom.

### Magnetism

Magnetic measurements were conducted on a Quantum Design MPMS-XL SQUID magnetometer using a 7 T superconducting magnet. The diamagnetic contribution of the polypropylene bag used to hold the sample was subtracted from the raw data, and the core diamagnetic contributions of the sample were accounted for using Pascal's constants.[4]

Compounds **1** and **2** were analyzed for DC susceptibility under a 1000 Oe applied field from 300 K to 2 K. Reduced magnetization measurements were performed from 2 K to 7 K at magnetic fields ranging from 1 T to 7 T. AC susceptibility measurements were made under an applied DC field of 0 Oe using an AC drive amplitude of 2 Oe at frequencies of 10 Hz, 100 Hz, 200 Hz, 500 Hz, and 1000 Hz from 10 K to 2 K in 1 K increments. AC susceptibility measurements were also made at frequencies ranging from 1 Hz to 1000 Hz between 2 K and 4 K in 0.1 K increments.

## Results

### Crystallographic Refinement Details

#### **1**·3.8$C_6H_{14}$

The asymmetric unit of **1**·3.8 $C_6H_{14}$ contains one molecule of **1** and 3.8 solvate molecules of hexane. Multiple instances of positional disorder are present in the structure. *t*Bu groups C4, C8, C19, C26, C30, C36, C52, and C63 are positionally disordered over two positions (major component occupancies: 71.5(17)%, 73.7(15)%, 72(2)%, 57(3)%, 72(5)%, 68(5)%, 81(2)%, 75.5 (13)%. *t*Bu group C41 is positionally disordered over three positions (occupancies: 40(3)%, 32(3)%, 28.0(12)%). Pivaloyl group O7 is disordered over two positions (major component occupancy: 68(5)%). Geometry and thermal parameter restraints were employed to ensure a chemically reasonable and computationally stable refinement.

There were several molecules of hexane in the structure that were located in the difference Fourier map. Multiple attempts to model these solvent molecules did not yield a successful and stable refinement. The electron density corresponding to these solvent molecules was removed using the SQUEEZE algorithm of PLATON.[5] PLATON calculated the void space to be 2254 Å$^3$ (22% of the total unit cell volume) and the total number of electrons removed was 768 electrons in the unit cell, corresponding to 3.8 molecules of hexane per molecule of **1** in the asymmetric unit.

***2**·2.5C$_5$H$_{12}$*

The asymmetric unit of **2**·2.5$C_5H_{12}$ consists of one unit of **2** and 2.5 molecules of $C_5H_{12}$ (Figure S1). *t*Bu group C20 is disordered over two positions (major component occupancy: 78.0(7)%). Pentane molecule C1S is disordered over a crystallographic inversion center (occupancy: 50%). Pentane molecule C6S is positionally disordered over two positions (major component occupancy: 80.1(9)%). Pentane molecule C11S is disordered over three positions (occupancies: 41.3(3)%, 38.2(3)%, 20.5(3)%). Bond distance and thermal parameter restraints were used to obtain a chemically reasonable and computationally stable refinement of these disordered moieties.

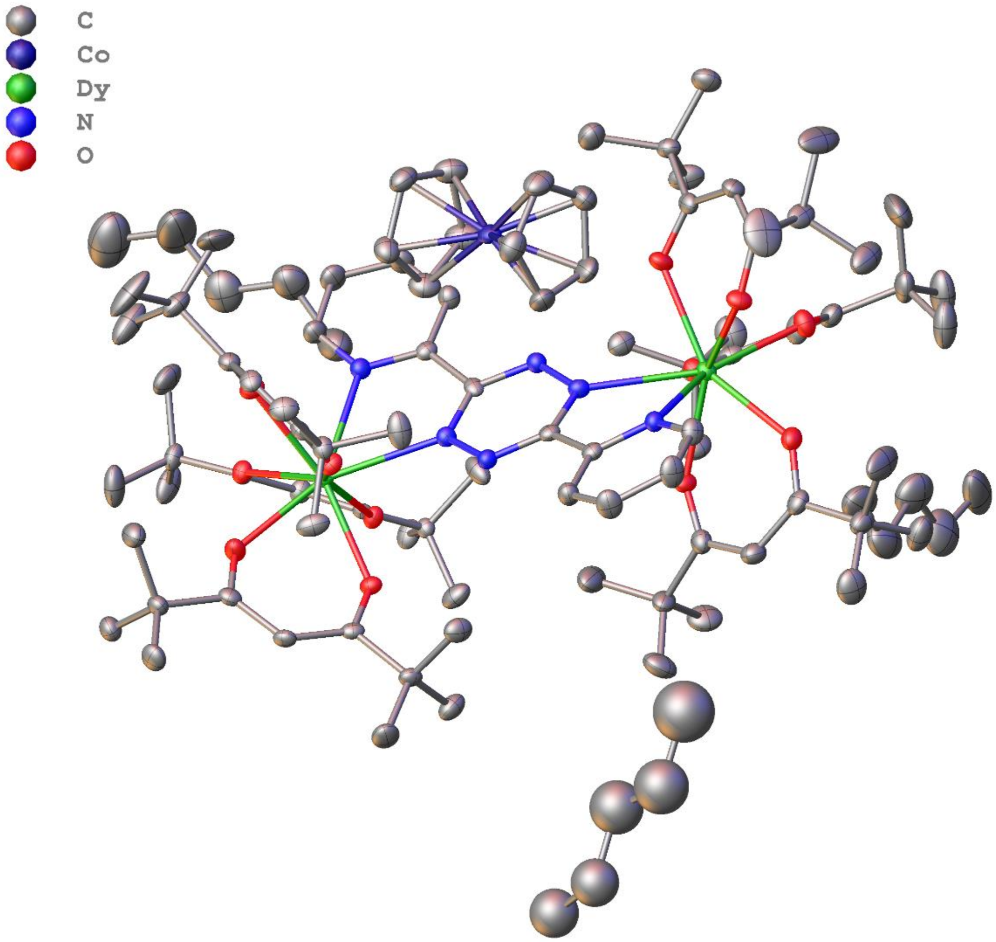

**Figure S1.** The asymmetric unit of **2**, excluding all hydrogen atoms and disordered components. All atoms are drawn as 50% thermal probability ellipsoids.

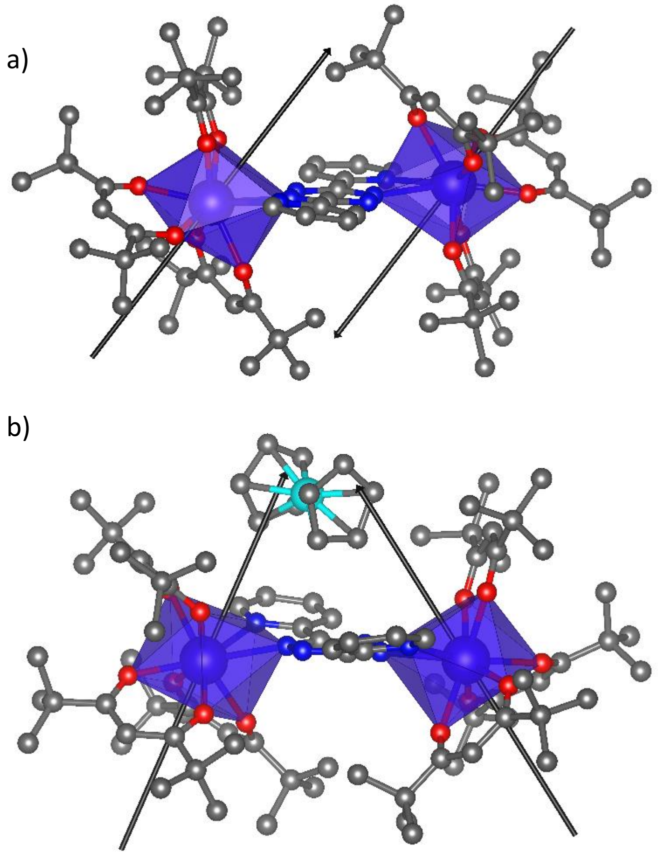

**Figure S2.** The crystal structures of a) 1 and b) 2, showing the coordination polyhedra of the Dy atoms in each compound. *The black arrows indicate the principal axis of the polyhedral.*

**Table S1** Crystal data and structure refinement for **1** and **2.**

| Identification code | **1** | **2** |
|---|---|---|
| Empirical formula | $C_{78}H_{122}Dy_2N_6O_{12}$ | $C_{100.5}H_{162}CoDy_2N_6O_{12}$ |
| Formula weight | 1660.81 | 2030.28 |
| Temperature/K | 100.0 | 110.0 |
| Crystal system | orthorhombic | monoclinic |
| Space group | $P2_12_12$ | $P2_1/c$ |
| a/Å | 17.7662(11) | 18.4756(6) |
| b/Å | 34.295(2) | 22.8962(8) |
| c/Å | 16.3935(11) | 25.6356(9) |
| α/° | 90 | 90 |
| β/° | 90 | 101.4390(10) |
| γ/° | 90 | 90 |
| Volume/Å$^3$ | 9988.5(11) | 10629.0(6) |
| Z | 4 | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.104 | 1.269 |
| μ/mm$^{-1}$ | 1.533 | 1.602 |
| F(000) | 3440.0 | 4248.0 |
| Crystal size/mm$^3$ | 0.268 × 0.102 × 0.02 | 0.268 × 0.166 × 0.034 |
| Radiation | MoKα (λ = 0.71073) | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 4.344 to 51.508 | 4.81 to 51.484 |
| Index ranges | $-21 \le h \le 21$<br>$-41 \le k \le 38$<br>$-13 \le l \le 20$ | $-22 \le h \le 22$<br>$-27 \le k \le 27$<br>$-31 \le l \le 31$ |
| Reflections collected | 40542 | 203756 |
| Independent reflections | 18948<br>[$R_{int}$ = 0.0485, $R_{sigma}$ = 0.0952] | 20253<br>[$R_{int}$ = 0.0552, $R_{sigma}$ = 0.0311] |
| Data/restraints/parameters | 18948/1186/1273 | 20253/192/1229 |
| Goodness-of-fit on F$^2$ | 1.030 | 1.029 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0545<br>$wR_2$ = 0.1052 | $R_1$ = 0.0302<br>$wR_2$ = 0.0582 |
| Final R indexes [all data] | $R_1$ = 0.0803<br>$wR_2$ = 0.1133 | $R_1$ = 0.0444<br>$wR_2$ = 0.0623 |
| Largest diff. peak/hole / e Å$^{-3}$ | 1.33/-1.56 | 2.82/-1.11 |
| Flack parameter | 0.478(15) | N/A |

## Magnetism

### *Compound 1*

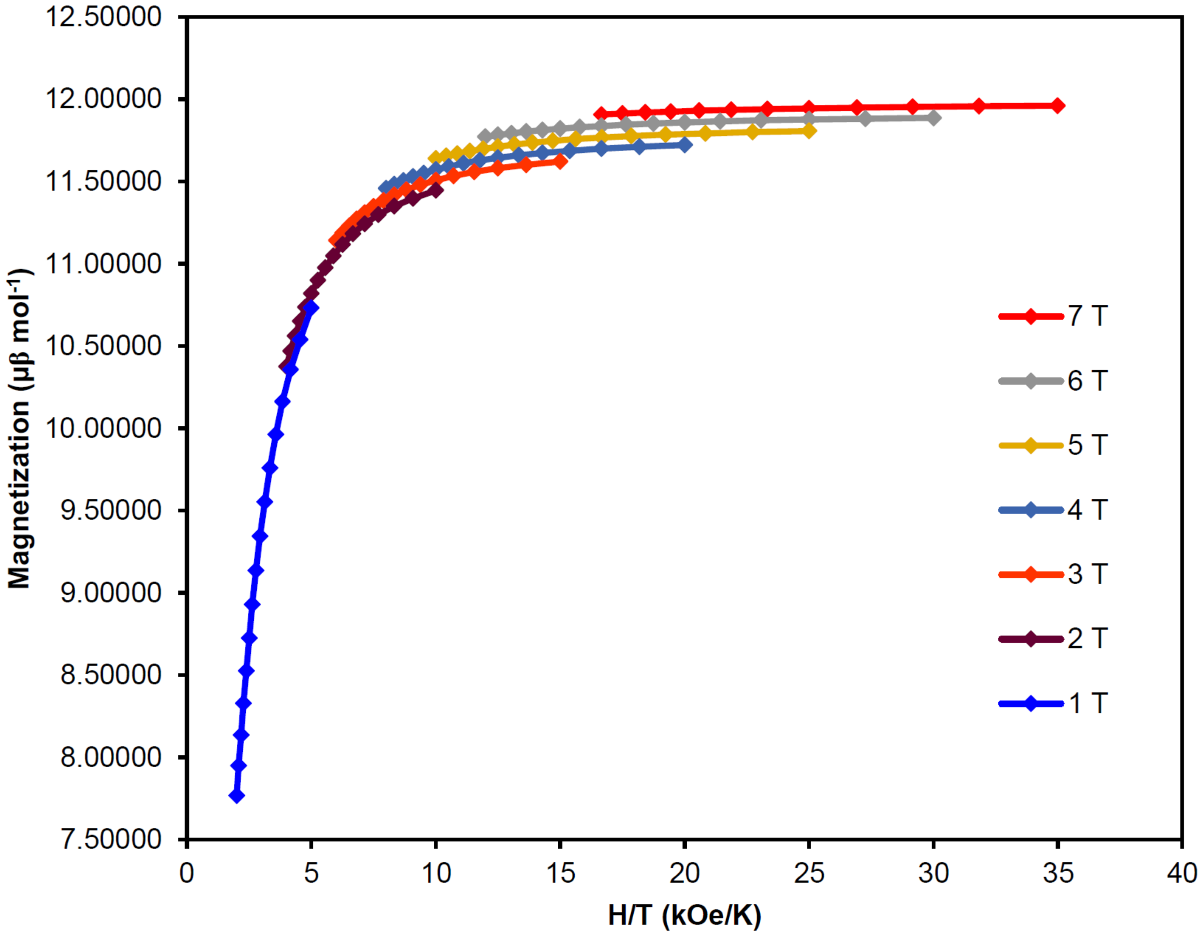

**Figure S3.** The reduced magnetization for **1**.

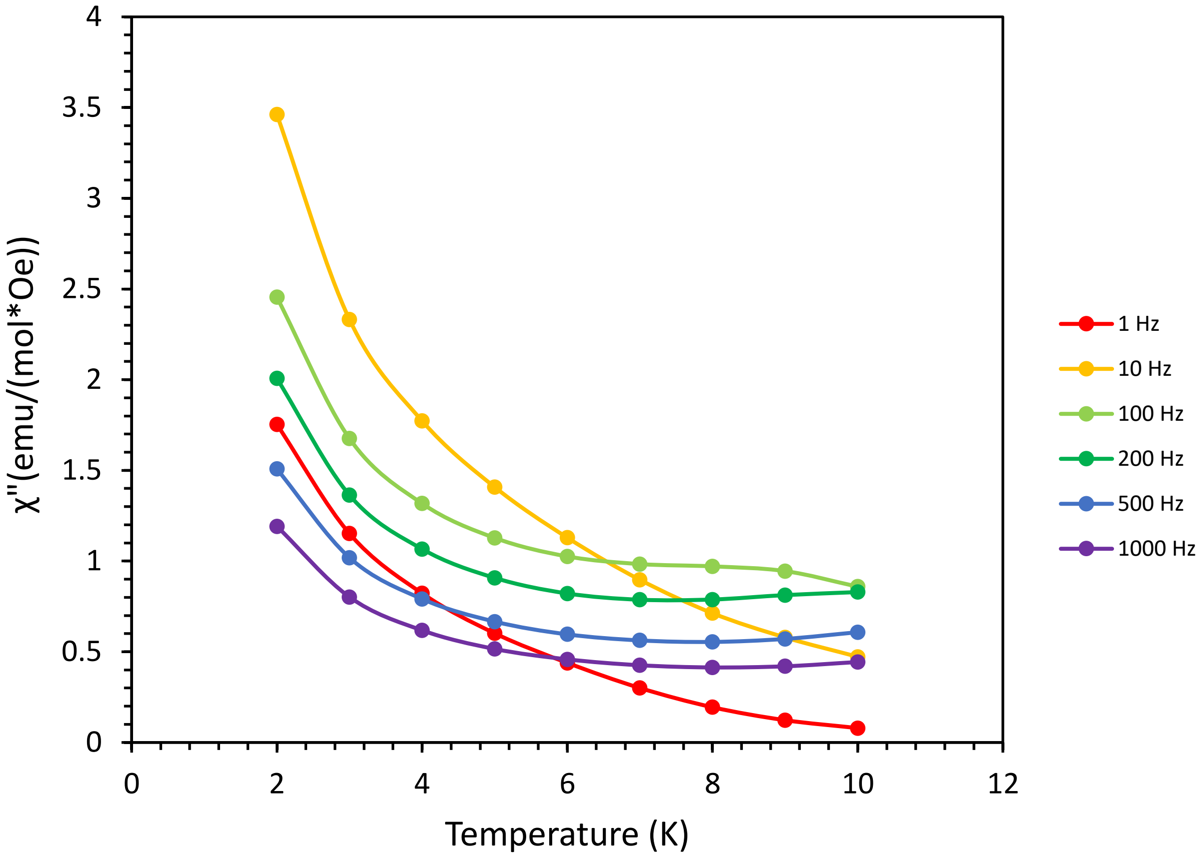

**Figure S4.** The plot of χ” vs. T for **1**. The lines are a guide for the eye.

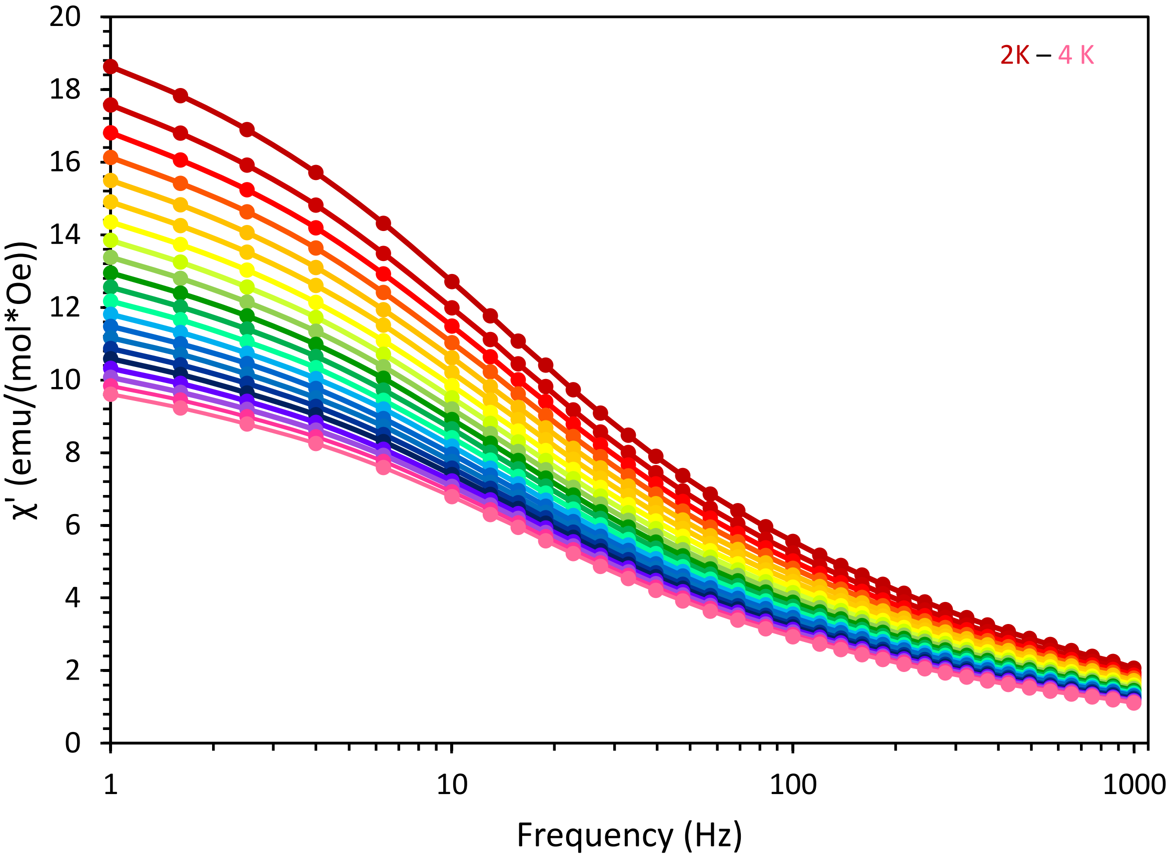

**Figure S5.** The χ’ vs. frequency AC susceptibility plot for **1**. The lines are a guide for the eye.

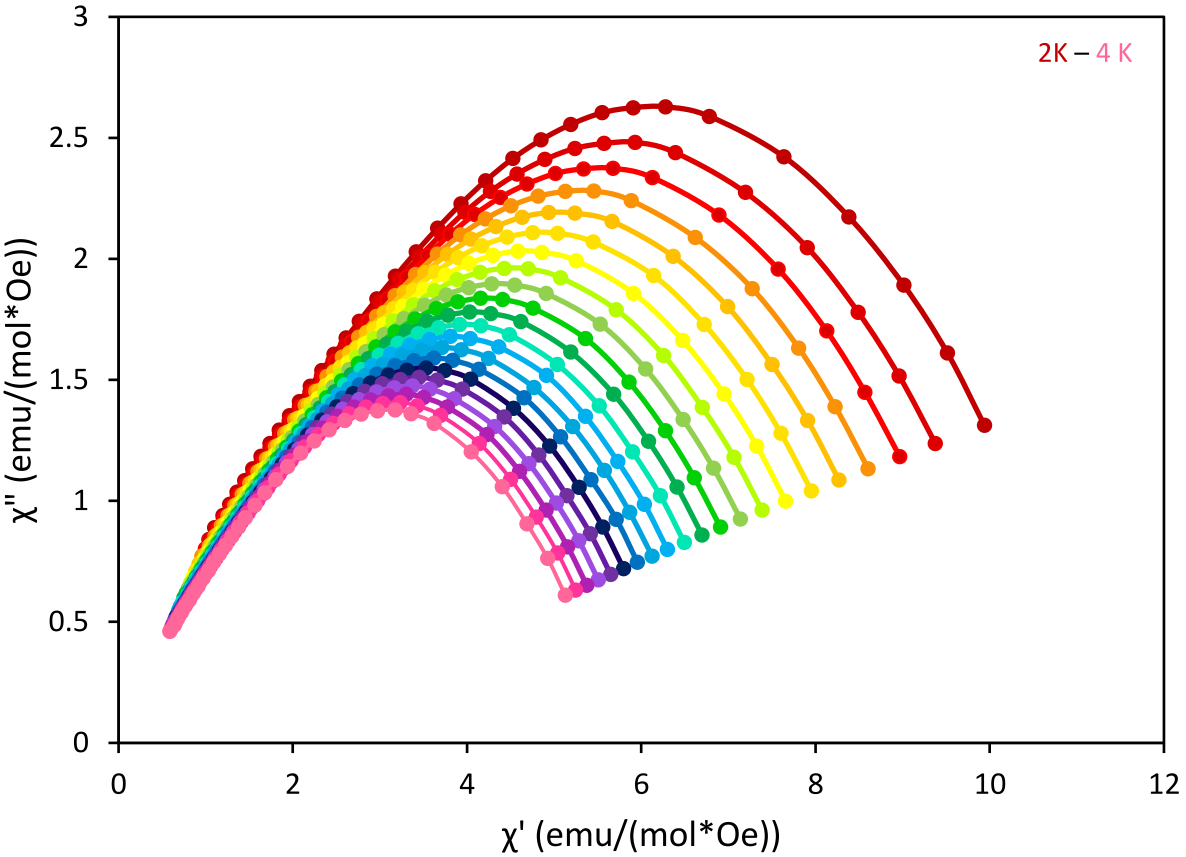

**Figure S6.** The Cole-Cole Plot for **1** from 2 K to 4 K. The lines are a guide for the eye.

*Compound 2*

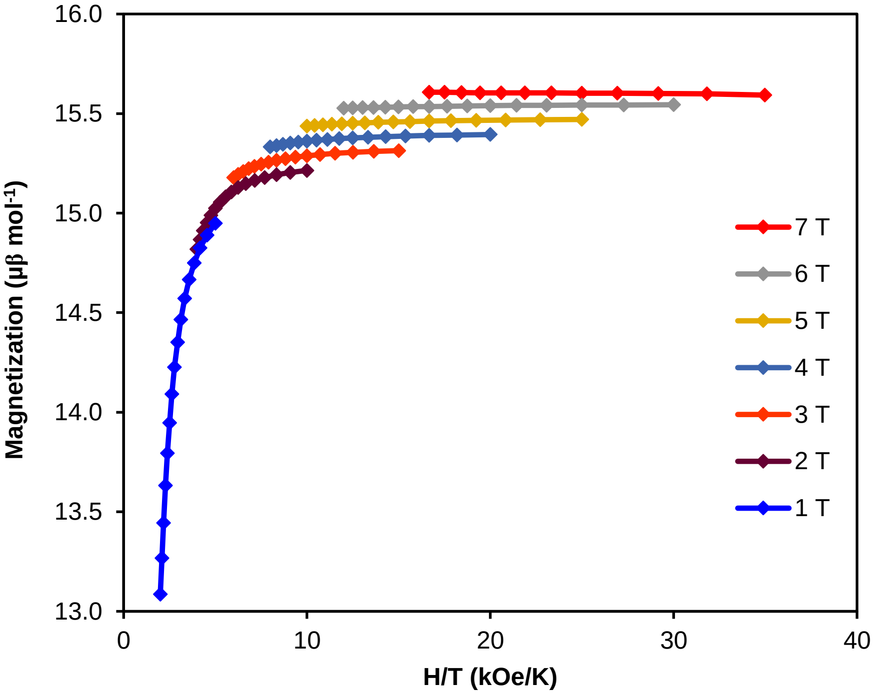

**Figure S7.** The reduced magnetization of **2**.

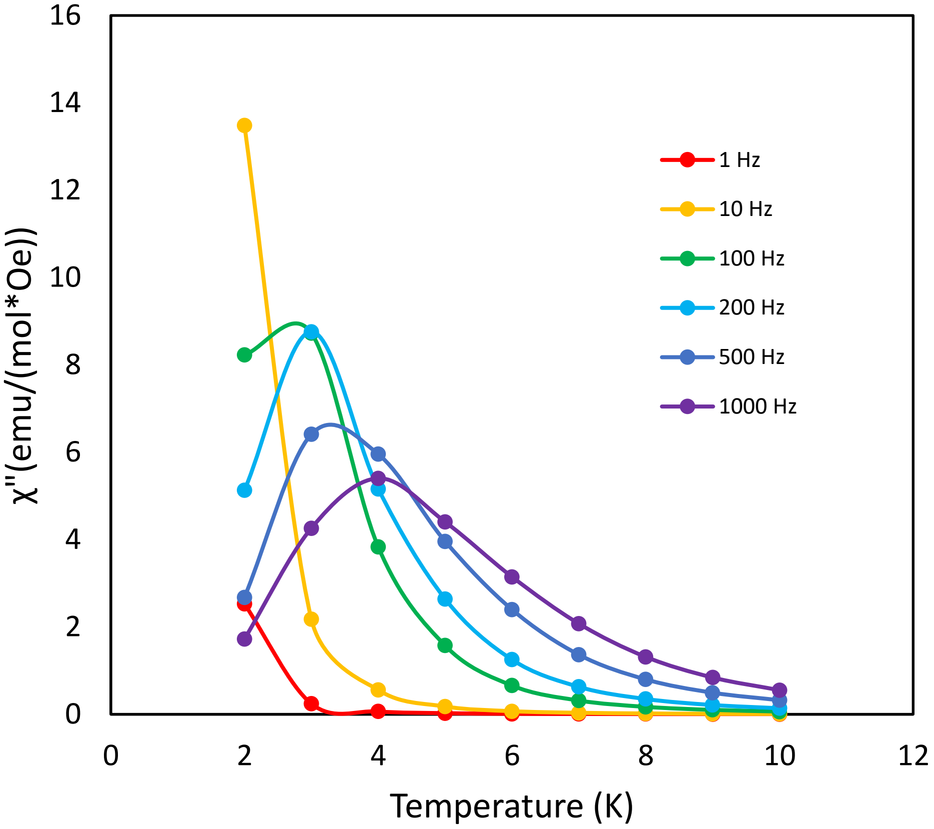

**Figure S8.** The plot of χ″ vs. T for **2**. The lines are a guide for the eye.

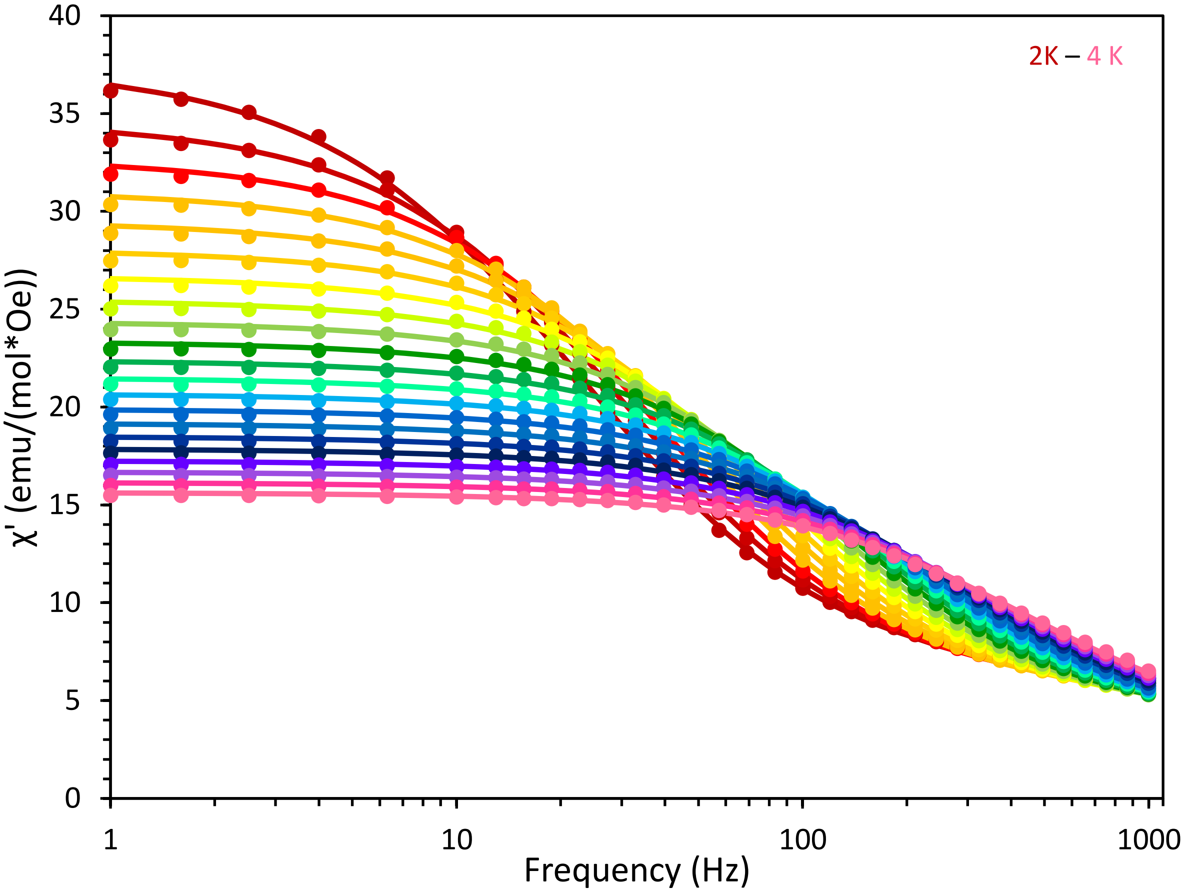

**Figure S9.** The χ' vs. Frequency plot for **2**. *The lines are fit using CC-fit.*

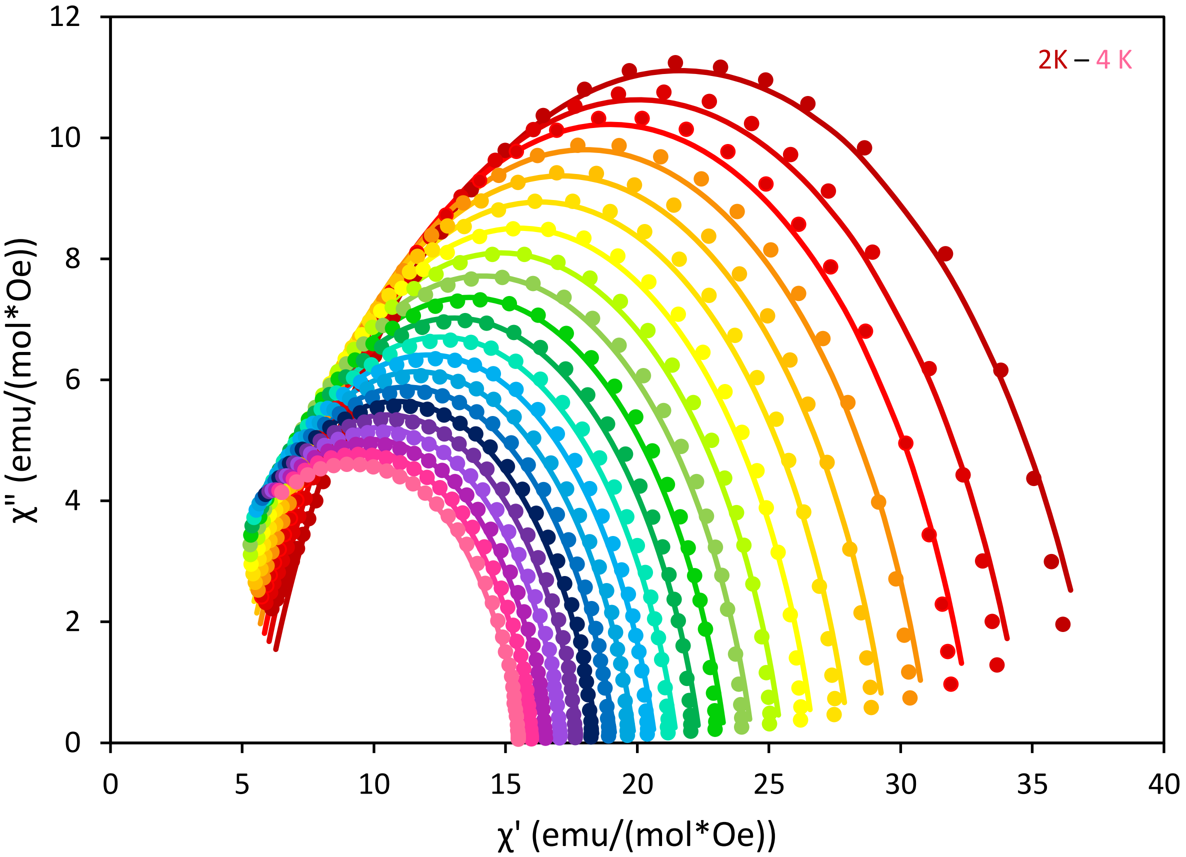

**Figure S10.** The Cole-Cole plot of **2**.

**Table S2.** The α and τ values calculated from fitting the Cole-Cole plot of **2**.

| Temperature (K) | τ (s) | α |
|---|---|---|
| 2.0 | 7.92E-03 | 1.62E-01 |
| 2.1 | 5.73E-03 | 1.50E-01 |
| 2.2 | 4.55E-03 | 1.45E-01 |
| 2.3 | 3.69E-03 | 1.45E-01 |
| 2.4 | 3.01E-03 | 1.46E-01 |
| 2.5 | 2.48E-03 | 1.50E-01 |
| 2.6 | 2.06E-03 | 1.54E-01 |
| 2.7 | 1.73E-03 | 1.60E-01 |
| 2.8 | 1.47E-03 | 1.66E-01 |
| 2.9 | 1.26E-03 | 1.72E-01 |
| 3.0 | 1.09E-03 | 1.78E-01 |
| 3.1 | 9.42E-04 | 1.84E-01 |
| 3.2 | 8.22E-04 | 1.90E-01 |
| 3.3 | 7.21E-04 | 1.95E-01 |
| 3.4 | 6.37E-04 | 1.99E-01 |
| 3.5 | 5.66E-04 | 2.02E-01 |
| 3.6 | 5.06E-04 | 2.04E-01 |
| 3.7 | 4.55E-04 | 2.06E-01 |
| 3.8 | 4.11E-04 | 2.06E-01 |
| 3.9 | 3.74E-04 | 2.05E-01 |
| 4.0 | 3.42E-04 | 2.03E-01 |

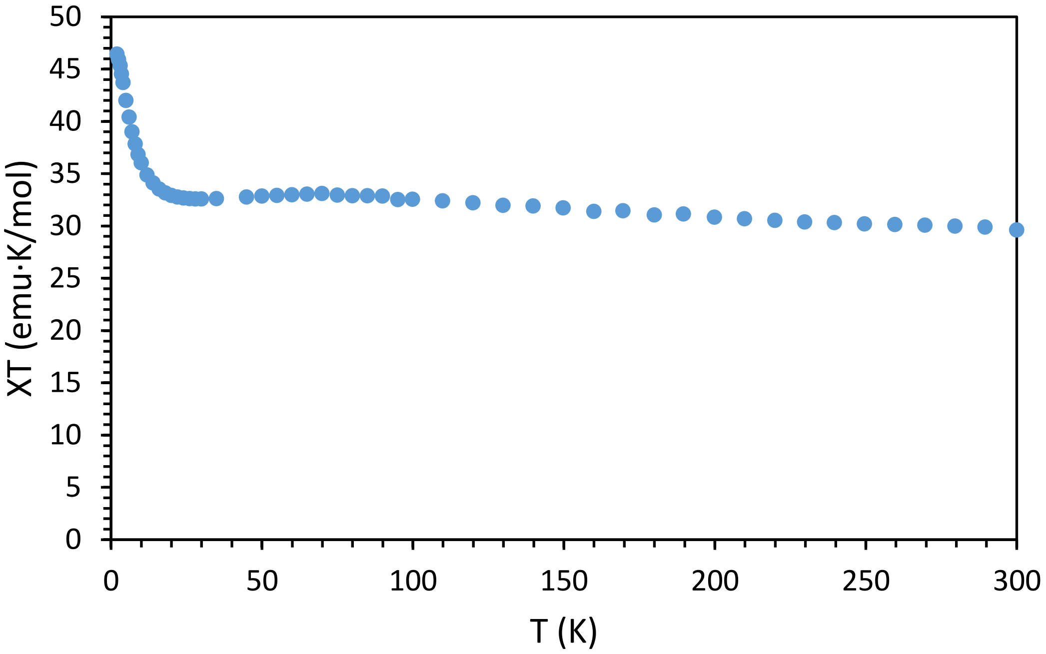

**Figure S11.** The magnetic susceptibility of **2** after 17 days of exposure to the atmosphere.

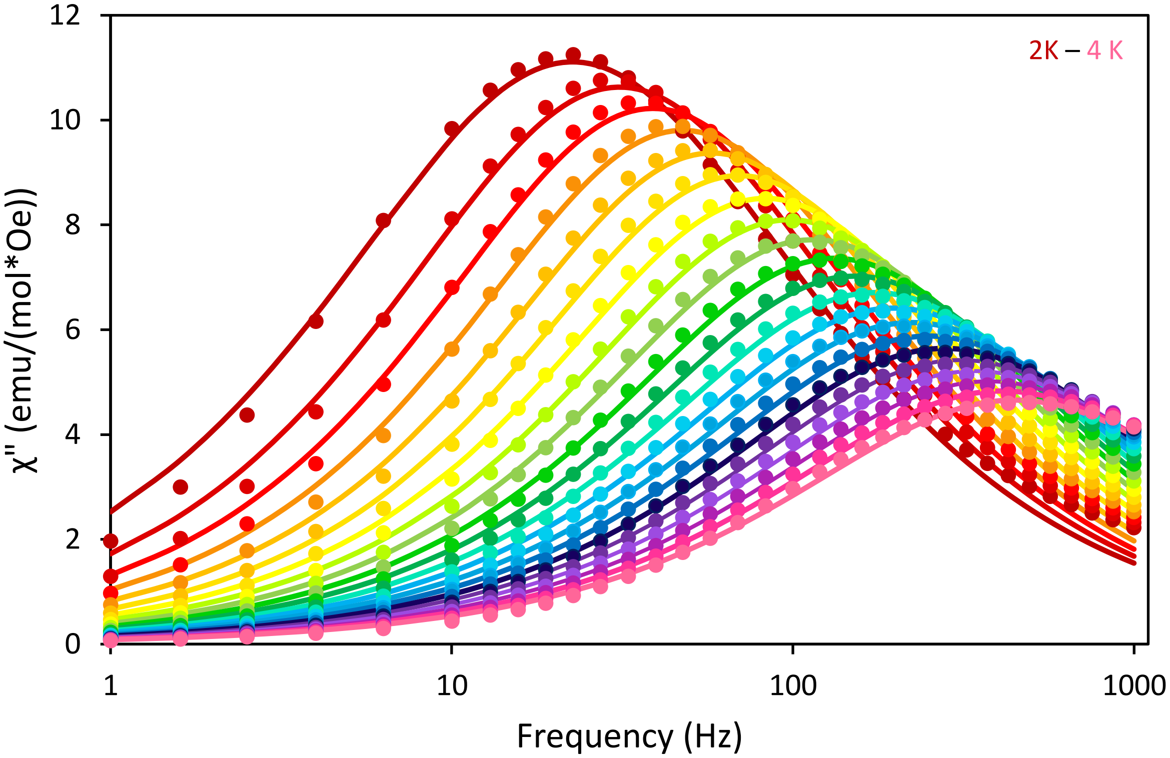

**Figure S12.** The χ” vs. Frequency plot for **2** after 17 days exposure to the atmosphere.

## References

1. Bruker-AXS, Journal, 2015.

2. G. M. Sheldrick, Acta Crystallographica Section A, Foundations and Advances, 2015, **71**, 3-8.

3. (a) G. M. Sheldrick, Acta crystallographica. Section C, Structural chemistry, 2015, **C71**, 3-8; (b) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, J. Appl. Crystallogr., 2009, **42**, 339-341.

4. G. A. Bain and J. F. Berry, J. Chem. Ed., 2008, **85**, 532-536.

5. A. L. Spek, Acta Crystallogr C Struct Chem, 2015, **71**, 9-18.