

### Supporting Information

#### Spontaneous Ligand Nitrosation and Self-Assembly into a Pentacopper Metallacrown Complex

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#### 1. Experimental

**Apparatuses and Measurements.** NMR spectra were taken on a 400 MHz JEOL ECX 400 spectrometer. X-ray photoemission spectroscopy (XPS) was taken on a Shimadzu ESCA-3400 (X ray source: Mg K $\alpha$ , 1253.6 eV). IR spectra were taken on a PerkinElmer SpectrumOne spectrometer using KBr pellets. Thermogravimetric analysis was conducted on a Rigaku ThermoPlus TG8120 apparatus with a scan rate of 5 °C min<sup>-1</sup>. Differential scanning calorimetry (DSC) measurements were performed using a Mettler-Toledo hot stage controller and a DSC microscopy cell with a scan rate of 5 °C min<sup>-1</sup>. Electrospray mass spectra (ESI-MS) were taken on an Agilent G1969A mass spectrometer. Typical conditions were as follows: flow rate: 0.5 mL min<sup>-1</sup>; ion polarity: positive; fragmentor: 70 V; skimmer: 40 V. Samples for MS was prepared by dissolving the crystals in H<sub>2</sub>O or CH<sub>3</sub>OH with the help of sonication, followed by filtration. Powder X ray diffraction was measured on a PANalytical X'Pert PRO MPD diffractometer in a reflection mode. Characterization of magnetization was carried out on a Quantum Design MPMS3 SQUID magnetometer with the VSM mode (sensitivity: 5 × 10<sup>-8</sup> emu). About 15 mg of the pulverized crystals wrapped in aluminium foil was used as the sample. The contribution of the aluminium foil to magnetization was subtracted by measuring the foil alone under the same conditions. Elemental analyses were performed by the Centre for Creative Materials Research, College of Science and Technology, Nihon University.

**Materials.** All chemicals were used as received. Cu(NO<sub>3</sub>)<sub>2</sub> · 3H<sub>2</sub>O (>99.0%) was purchased from Wako Pure Chemical Industries. Acetylacetonedioxime was purchased from Tokyo Chemical Industry. All aqueous solutions were prepared with Milli Q water (Merck Millipore Direct-Q UV3, 18.2 M $\Omega$  cm resistivity).

**Single Crystal X-Ray Analysis.** The single crystal diffraction analysis data were collected at 93 K with a Rigaku VariMax Dual with a Saturn diffractometer using Mo K $\alpha$  radiation (0.71075 Å). The structures were solved by direct method using SHELXT-2015<sup>1</sup> and refined by the full-matrix least-squares method using SHELXL-2014/7,<sup>2</sup> with the help of graphical interface supplied by ShelXle (rev 769)<sup>3</sup> and OLEX2.<sup>4</sup>

Hydrogen atoms are allowed to ride on the bonded atoms. Each of the nitroso groups are assumed to be disordered between two positions with 50%/50% occupancies. Otherwise no restraint/constraint was applied to the nitroso groups. Each ligand (LH<sub>3</sub> = CH<sub>3</sub>(CNOH)<sub>3</sub>CH<sub>3</sub> = C<sub>5</sub>H<sub>9</sub>N<sub>3</sub>O<sub>3</sub>) was assumed to be doubly deprotonated on average to give a dianion (LH<sup>2-</sup> = C<sub>5</sub>H<sub>7</sub>N<sub>3</sub>O<sub>3</sub>). Hence the crown framework consisting of four ligands and four peripheral Cu<sup>2+</sup> is neutral. The charge of the core Cu1 is thus compensated by NO<sub>3</sub><sup>-</sup> ions. The refined site occupancy for Cu1 were 0.68–0.78 for different batches of single crystals. The cif file submitted and detailed discussion in the text are for the crystal with the site occupancy of 0.78.

The void space is disordered but the electron densities suggested two positions for NO<sub>3</sub><sup>-</sup> ions and three positions for H<sub>2</sub>O molecules. One of the NO<sub>3</sub><sup>-</sup> ions (N8O<sub>3</sub> = N8, O11, O12, O13) and H<sub>2</sub>O17 are situated at the same position close to an inversion centre. These moieties are thus assumed to be disordered between the two positions each related by the inversion centre with 50%/50% occupancies. Another position was found to be occupied either by the other NO<sub>3</sub><sup>-</sup> ion (N9O<sub>3</sub> = N9, O14, O15, O16) or two H<sub>2</sub>O molecules (H<sub>2</sub>O18 and H<sub>2</sub>O19).

The fractions of the set of atoms (NO<sub>3</sub> or 2 H<sub>2</sub>O) should be determined by the requirement of charge neutrality, which is interrelated with the occupancy of Cu1. The SUMP command in Shelxl was used to make a consistent structural model incorporating the charge balance, but in the final rounds of Shelxl, the site occupancy values were fixed to the refined values.

Explicitly, the proposed structure model has been obtained by refinement with the charge balance between

positive charge:  $4 \times (+2, \text{Cu}_{\text{peripheral}}) + n \times (+2, \text{Cu1})$

and

negative charge:  $4 \times (-2, \text{LH}) + 1 \times (-1, \text{N8O}_3) + m \times (-1, \text{N9O}_3)$

being kept by putting a restraint:

$$2n = 1 + m$$

where  $n$  and  $m$  are the numbers of atoms/molecules for

$n \text{ Cu1}$  and  $2n \text{ H}_2\text{O8}$

and

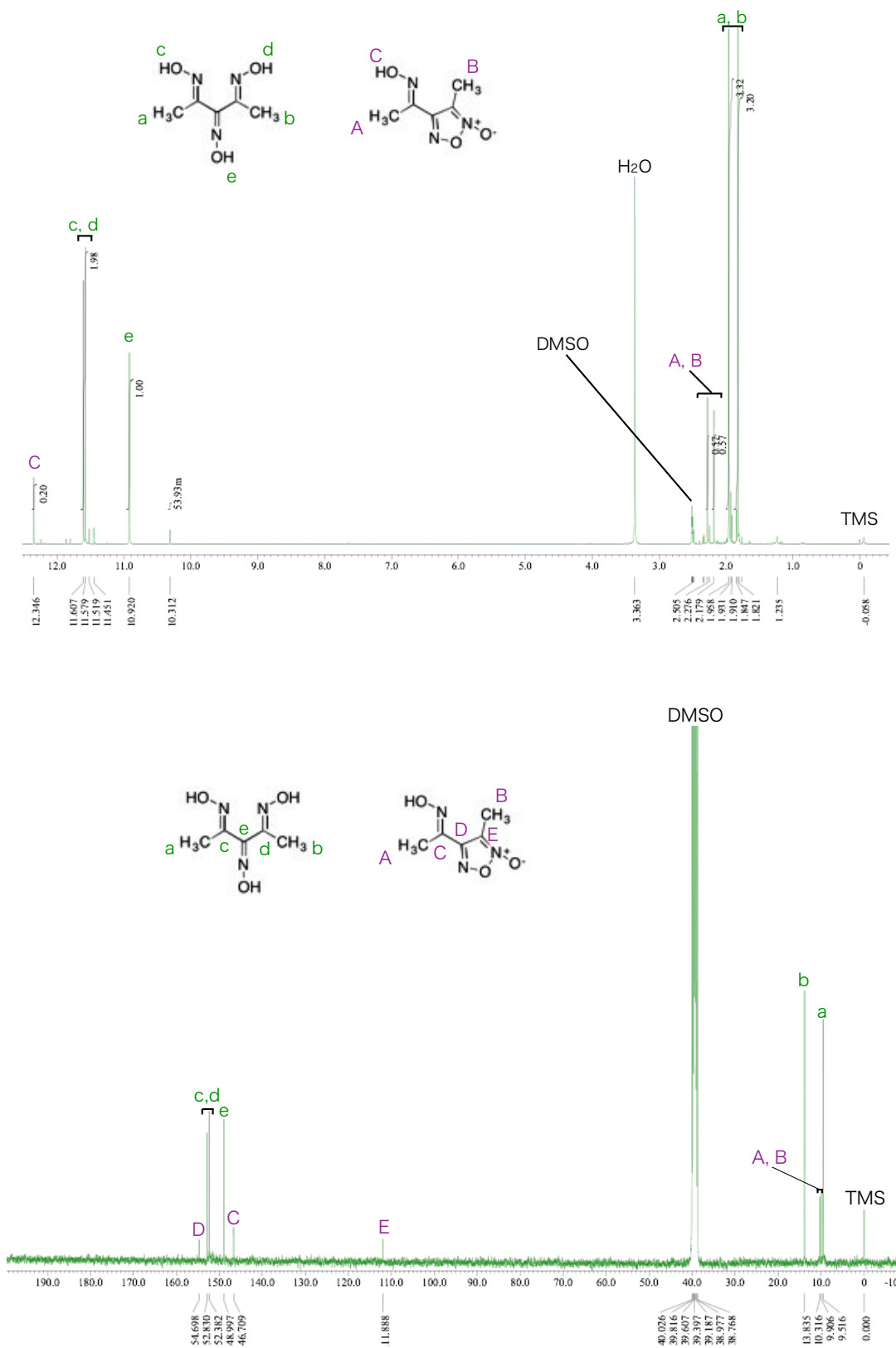
$m \text{ N9O}_3$ ,  $(1-m) \text{ H}_2\text{O18}$  and  $(1-m) \text{ H}_2\text{O19}$ ,

Here,  $\text{H}_2\text{O8}$  is a water molecule coordinating to  $\text{Cu1}$  and  $\text{H}_2\text{O18}$  and  $\text{H}_2\text{O19}$  are water molecules occupying the same site with  $\text{N9O}_3$ . For the crystal reported in the text, the values  $n = 0.78$  and  $m = 0.56$  were obtained, leading to the charge balance:

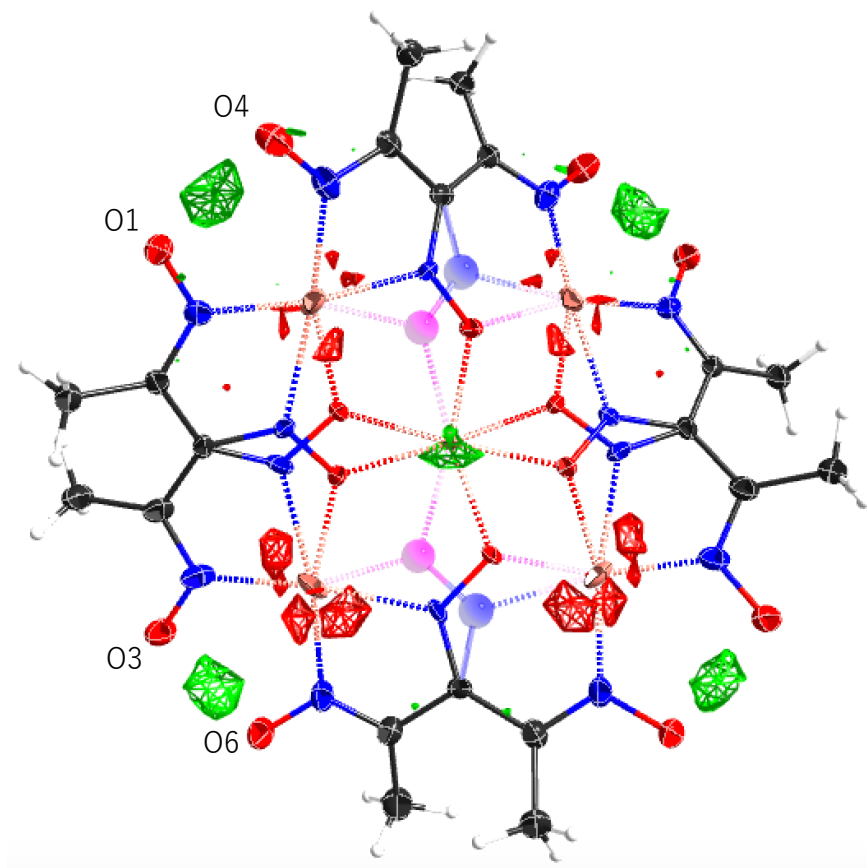
$$4.78 \times (+2, \text{Cu}) = 4 \times (-2, \text{LH}) + 1.56 \times (-1, \text{NO}_3).$$

To check the validity of the structure model, we also refined the structure *without any restraint on the charge balance*. The site occupancies  $n$  and  $m$  were refined *independently*, removing the condition  $2n = 1 + m$ . Fig. S8 shows the sum of positive and negative charges based on the  $m$  and  $n$  values thus obtained for four crystals taken from four different solutions, including the one reported in the text. It is clear from the figure that crystals refined to have less  $\text{Cu1}$  (less positive charge) tend to be refined to have less  $\text{N9O}_3$  (less negative charge), and vice versa, such that *the charge balance is maintained without a priori restraint on the charge balance* within  $\leq 0.1$  per volume twice the asymmetric unit, i.e., per metallacrown. This result clarifies the charge balance, lending further support to the proposed structure model.

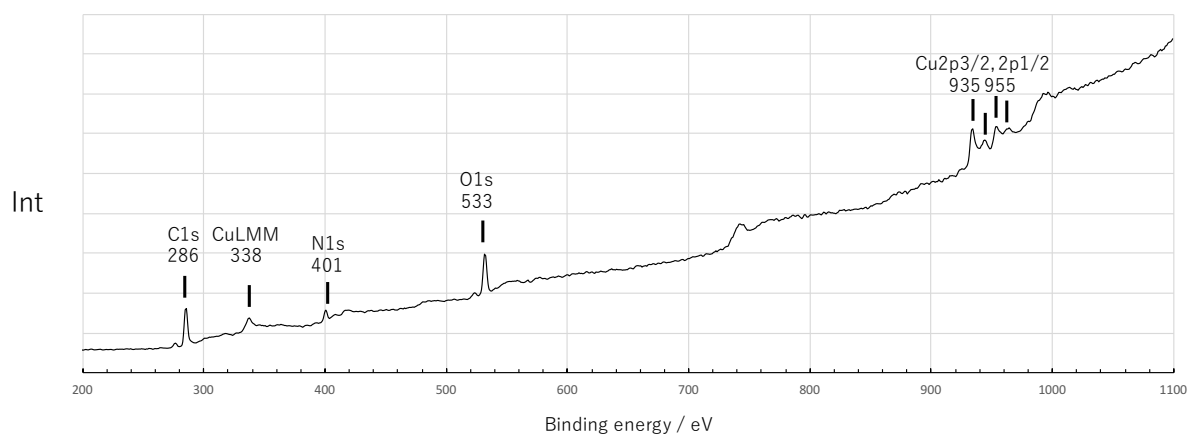
## 2. Supporting Figures



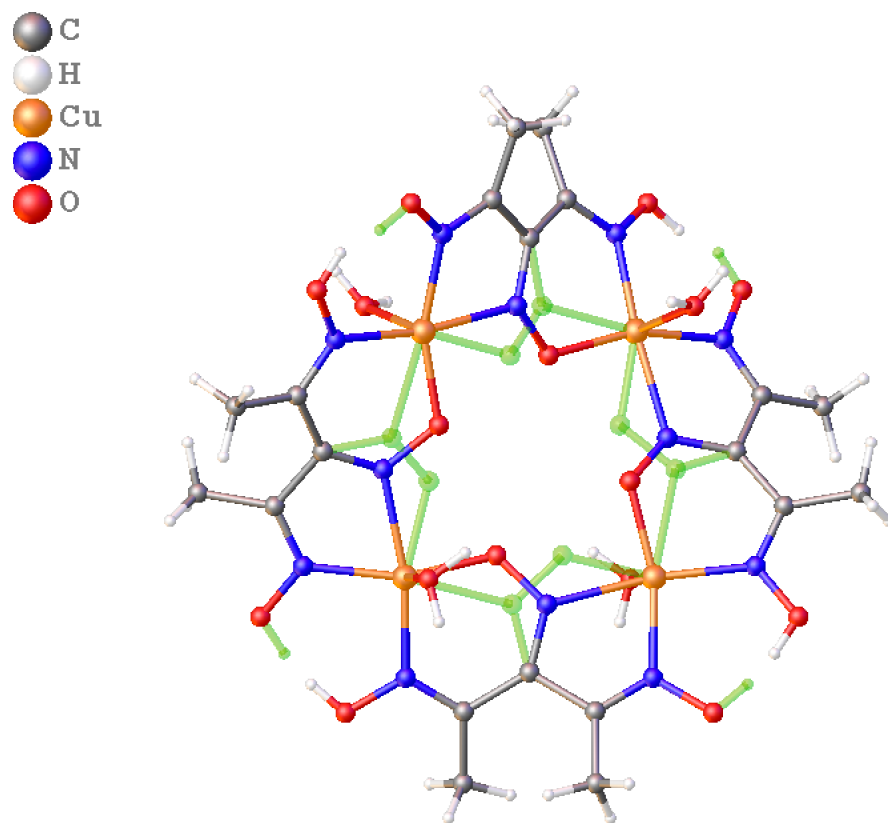
**Fig. S1** NMR spectra for the ligand after removing Cu atoms from the crystals in  $d_6$ -DMSO. Top:  $^1\text{H}$ . Bottom:  $^{13}\text{C}$ .



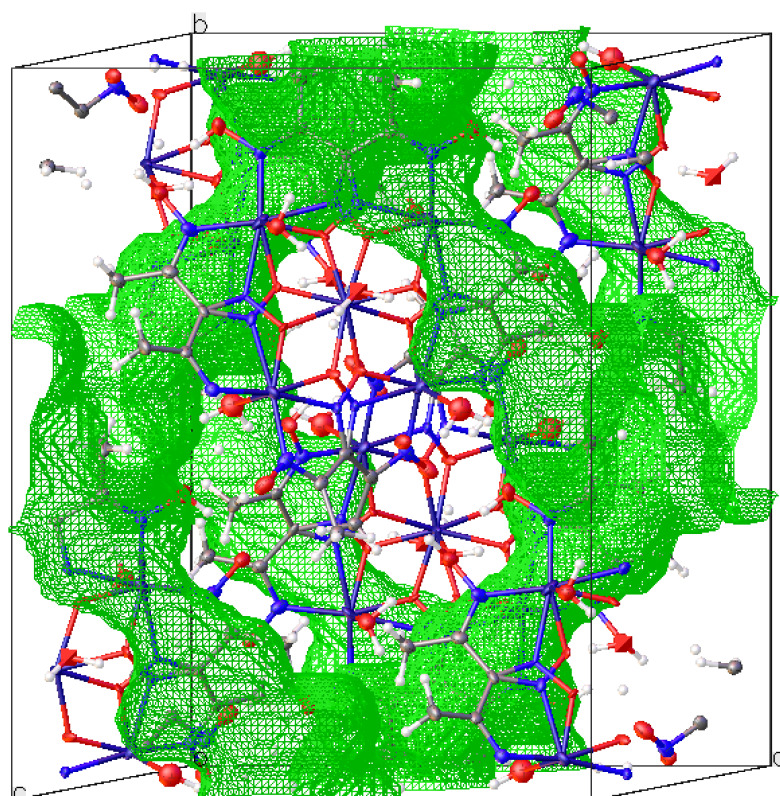
**Fig. S2** Crystal structure of the pentacopper metallacrown complex, modelled without the peripheral oxime hydrogens. Excess electron density regions between the oxime oxygen atoms (green mesh) are indicated by ShelXle. Ellipsoids show 50% probability.  $\text{NO}_3^-$  and  $\text{H}_2\text{O}$  are omitted for clarity.



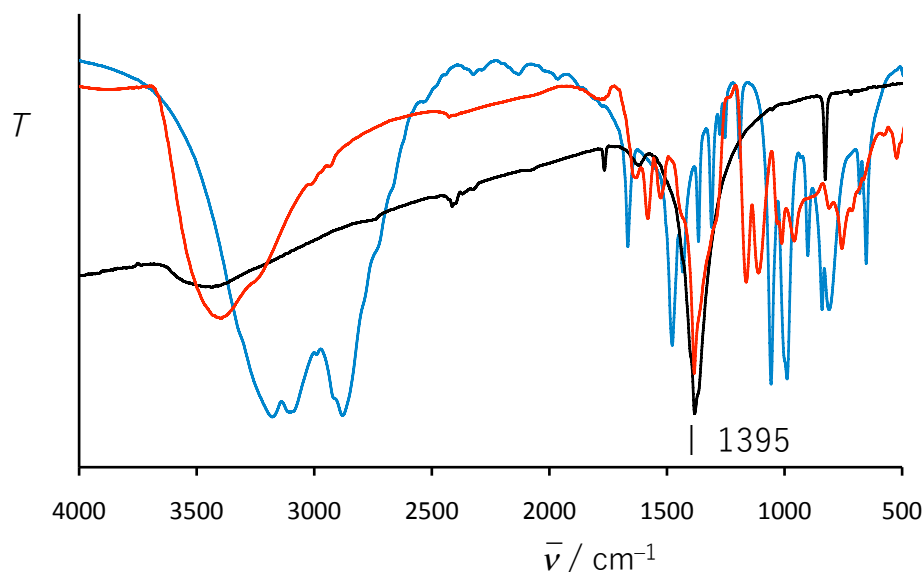
**Fig. S3** XPS survey spectrum for the pentacopper complex.



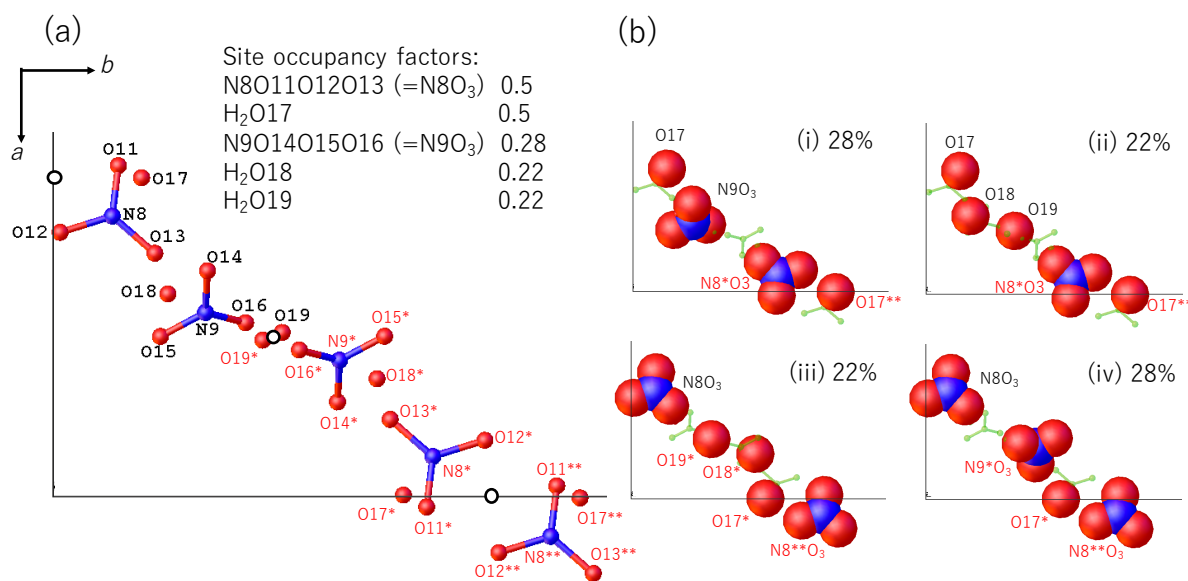
**Fig. S4** Metallacrown complex with an empty core, which accounts for 22% of the complexes in the crystal.



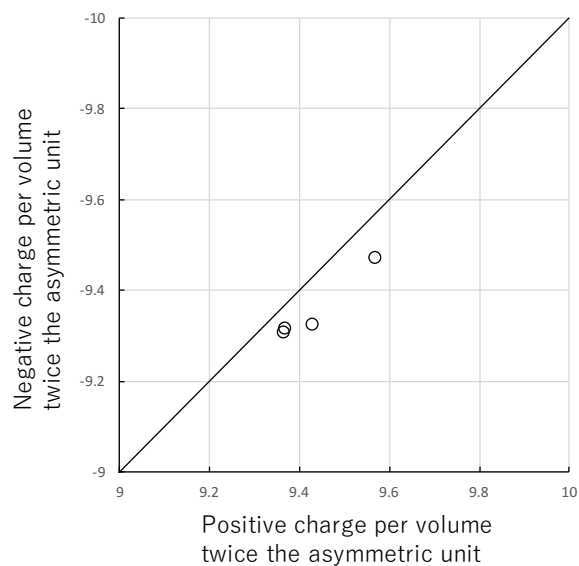
**Fig. S5** Disordered region which is filled by  $\text{NO}_3^-$  ions and noncoordinating  $\text{H}_2\text{O}$  molecules.



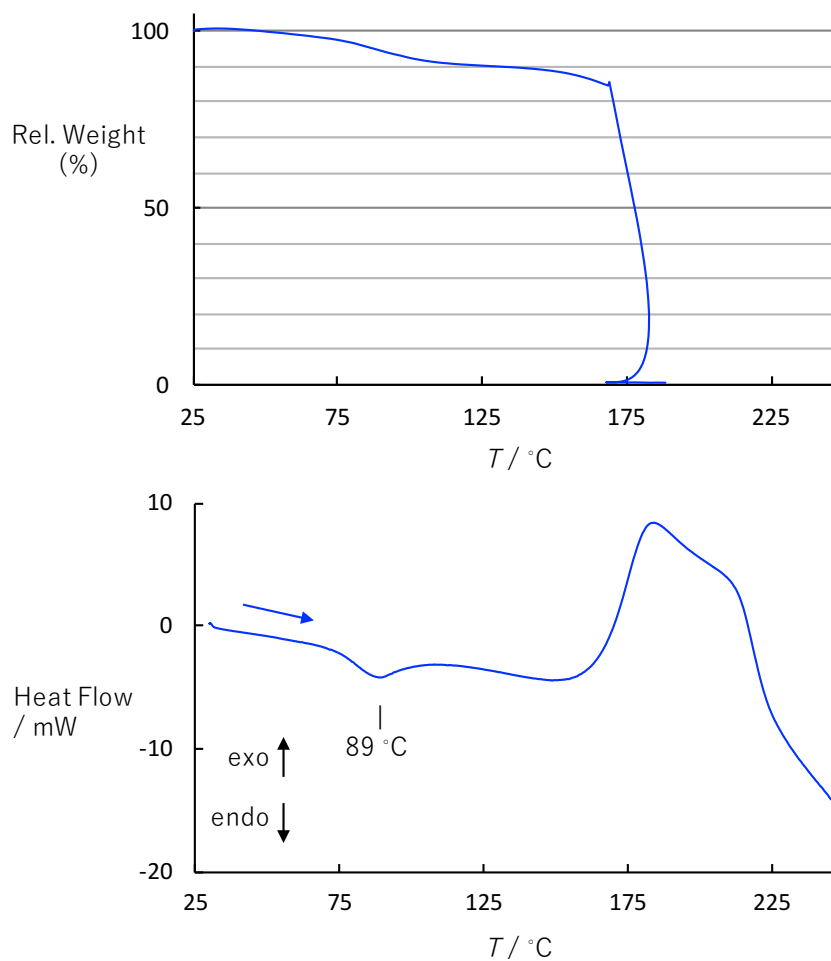
**Fig. S6** IR spectra (KBr) of acetylacetonedioxime (blue),  $\text{Cu}(\text{NO}_3)_2$  (black), and the crystals (red).



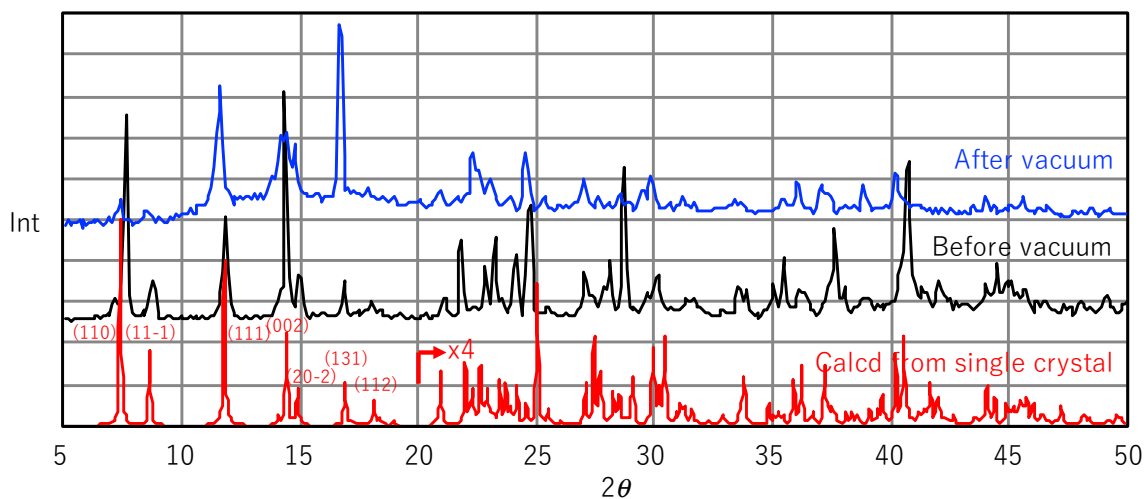
**Fig. S7** Disordered  $\text{NO}_3^-$  ions and noncoordinating  $\text{H}_2\text{O}$  molecules. (a) All positions. The open circles indicate inversion centres. The region between two inversion centres corresponds to an asymmetric unit. The starred labels in red indicate symmetry related atoms. (b) Possible packing patterns. The following explanation refers to the black-labelled atoms. One of the nitrate ions ( $\text{N8O}_3^-$ ) is situated at the same site with  $\text{H}_2\text{O17}$  near an inversion centre and thus the site occupancies are modelled as 50%/50%. When  $\text{H}_2\text{O17}$  is present, there is room either for another nitrate ion ( $\text{N9O}_3^-$ , 28%, i) or two water molecules ( $\text{H}_2\text{O18}$  and  $\text{H}_2\text{O19}$ , both 22%, ii) in the adjacent position in the same asymmetric unit. When  $\text{N8O}_3^-$  is present, however, there is no room in the adjacent position (iii and iv).



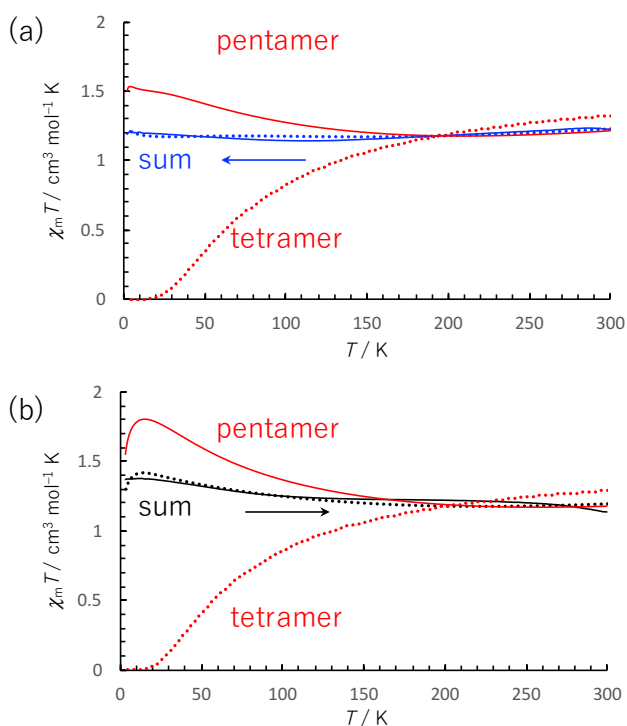
**Fig. S8** Positive and negative charges per volume twice the asymmetric unit refined without restraint on the charge balance for four different single crystals from four different solutions, including the one discussed in the text.



**Fig. S9** Thermal properties of the complex ( $5\text{ }^{\circ}\text{C min}^{-1}$ ). Top: TG (11.668 mg). The sample may have been blown off by the large exothermic reaction at  $175\text{ }^{\circ}\text{C}$ . Bottom: DSC (4.2 mg).

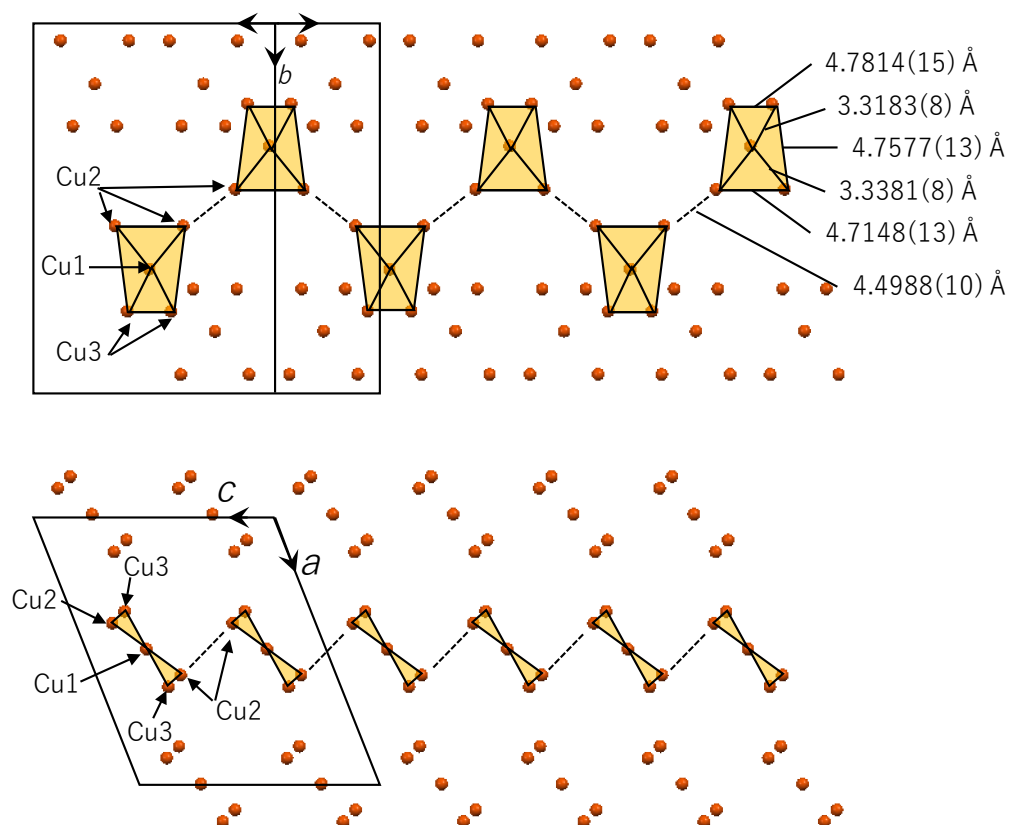


**Fig. S10** Comparison of powder X-ray patterns for samples measured before and after vacuum treatment and that calculated from the single crystal data.



**Fig. S11** Contributions of pentamer (red solid line) and tetramer (red dotted line) to the total  $\chi_m T$  (blue and black dotted lines). The solid lines are observed traces. The sum  $\chi_m T$  is obtained by  $0.78 \times \chi_m T$  (pentamer) +  $0.22 \times \chi_m T$  (tetramer). (a) Decreasing-temperature trace. (b) Increasing-temperature trace.





**Fig. S12** Arrangement of pentacopper complexes in the crystal and inter copper distances. The six pentamers are highlighted. Top: view perpendicular to the  $bc$  plane. Bottom: view along the  $b$  axis.

1. G. M. Sheldrick, *Acta Cryst. A*, 2015, **71**, 3–8.
2. G. Sheldrick, *Acta Crystal. A*, 2008, **64**, 112–122.
3. C. B. Hubschle, G. M. Sheldrick and B. Dittrich, *J. Appl. Crystallogr.*, 2011, **44**, 1281–1284.
4. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339–341.