# Peroxide-Templated Assembly of a Trimetal Neodymium Complex Single-Molecule Magnet

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**ABSTRACT:** In this work, we present a trimetal neodymium complex with two notable qualities. First, the assembly of the complex is templated by peroxide derived from atmospheric oxygen. Second, the bulk material behaves as a superparamagnet, implying that the individual complexes are molecular magnets. Peroxide-templated assembly is possible because of the confluence of the high oxophilicity of neodymium along with the use of an azeotropic distillation synthesis method, which excludes water but admits oxygen. SQUID magnetometry measurements show an extremely high magnetic susceptibility as well as a lack of remanence.

emplated assembly is a phenomenon in supermolecular and coordination chemistry in which the templating species has the principal effect of determining the geometry of another structure.<sup>1</sup> Examples are commonly differentiated from the more general structural effects of reagents by virtue of having a "small" impact on the chemistry of the system (noncovalent interactions) and the formation of similar systems of differing geometry in the absence of the template. Templated assembly has been studied for several decades for the preparation of mechanically interlinked structures such as rotaxanes and catenanes.<sup>1,2</sup> Much of the early work in the field focused on the interactions of metal cations with dipoles in organic molecules.<sup>3,4</sup> More recent attention has been paid to the use of anion templates because of their advantages in specificity and available ion geometries.<sup>5-8</sup> In some cases, templating anions can be derived from gases absorbed from the atmosphere, such as carbonate formed from CO<sub>2</sub> or the rarer example of peroxide derived from oxygen.<sup>9-11</sup> This latter case, which is the topic of this work, requires very oxophilic metals and the strict exclusion of moisture.

Anion-templated assembly is useful in the synthesis of complexes containing multiple metal centers, such as caging complexes, and has gained attention more recently.<sup>12,13</sup> Such structures are useful for applications in single-molecule magnets, where a large number of metal centers aid the synthesis of high-spin complexes.<sup>14,15</sup> Many of the reported lanthanide single-molecule magnets feature a central anion caged by a cluster of lanthanides in this manner.

We report here an unexpected complex that arose from efforts to synthesize a neodymium complex with a bis(2pyridinal)ethylenediimine ligand, which we had hoped would be useful for diene polymerization. The neodymium feedstock to produce this catalyst was neodymium chloride hexahydrate, and earlier efforts had revealed that the water of crystallization would problematically remain bound to the neodymium atom and prevent formation of the complex. While anhydrous neodymium chloride is available and conventional water-free methods would do just fine, we instead chose to use an expedient azeotropic distillation method to remove water during the synthesis. This method does not remove oxygen from the reaction, and this quality, along with an emerging water-free environment and the very oxophilic neodymium, created conditions appropriate for atmosphere-sourced peroxide-templated assembly. A crystal structure was obtained in which three neodymium atoms, each coordinated to one of the tetradentate ligands, arrange around a central peroxide ion. While this complex lacked the desired catalytic activity, the structure was sufficiently interesting to merit some further study. Superconducting quantum interference device magnetometry (SQUID) measurements revealed surprisingly high magnetic susceptibility, which is suggestive of superparamagnetism. Because superparamagnetism is the result of an ensemble of noninteracting ferromagnets, this, in turn, suggests that the individual clusters represent single-molecule magnets.<sup>16</sup>

Bis(2-pyridinal)ethylenediimine was synthesized using a previously reported modified method.<sup>17</sup> 2-Pyrdinecarboxaldehyde and diethyl ether were introduced to a dry round-bottom flask, and ethylenediamine was then added dropwise. Anhydrous magnesium sulfate was added to the flask to remove the water byproduct. The reaction mixture was stirred at room temperature for 4 h. A precipitate formed and was removed by filtration and recrystallized in a hexane/diethyl ether mixture, yielding a yellow solid. NMR and crystallographic characterization can be found in the Supporting Information and are in good agreement with previously reported results.<sup>18,19</sup>

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The neodymium complex  $[Nd_3Cl_6(L)_3(O)_2]Cl$  was synthesized by azeotropic distillation. A molar ratio of 1:2 for NdCl<sub>3</sub>. 6H<sub>2</sub>O and bis(2-pyridinal)ethylenediamine was used. NdCl<sub>3</sub>. 6H<sub>2</sub>O (1.00 g, 2.7 mmol) was dissolved in 20 mL of absolute ethanol. Bis(2-pyridinal)ethylenediamine (1.337 g, 5.4 mmol) was dissolved in 40 mL of toluene and then introduced to the flask. A distillation apparatus was assembled, and the reaction mixture was heated. The ternary azeotrope consisting of toluene, ethanol, and water started to boil off at 74.4 °C. After complete removal of the water of crystallization, the ligands were coordinated to the metal center. The binary ethanol/ toluene azeotrope was then removed at a temperature of 76.7 °C, followed by toluene at its boiling point of 110 °C. This method expediently produces a water-free environment without the need for an air-free technique and, importantly, allows the reaction to be exposed to oxygen. After complete removal of all of the solvent, a brown solid formed. This solid was redissolved in chloroform, and continued exposure to air prompted the precipitation of a light-brown solid, which can be recovered by centrifugation with chloroform washing. The precipitate was purified by a recrystallization method in methanol/pentane. After 3 weeks, single crystals were obtained via a slow vapor diffusion method with methanol and pentane at 0 °C. Notably, if far less exposure to oxygen is permitted, this reaction instead yields a monometallic  $[NdCl(L)(H_2O)_3]$ - $Cl_2 \cdot 2(H_2O)$  complex [L = bis(2-pyridinal)ethylenediamine], more information for which can be found in the Supporting Information.

Single-crystal X-ray diffraction data were collected on a Bruker D8 Quest Kappa single-crystal X-ray diffractometer, equipped with an I $\mu$ S microfocus source (Mo K $\alpha$ ,  $\lambda$  = 0.71073 Å), a PHOTON 100 CMOS detector, and an Oxford Cryostreams cryostat at 100 K. The intrinsic method was used for the initial structure model.<sup>20</sup> SHELXL-2014 was used to refine all non-hydrogen atoms.<sup>21</sup>

The crystal structure of the complex, shown in Figure 1, consists of a triangular array of neodymium atoms coordinating a peroxide anion. The atomic positions and thermal parameters are in Table S8. The peroxide anion is coordinated to three neodymium ions in a  $\mu_3$ - $\eta^2$ : $\eta^2$ : $\eta^2$  manner. The structure has 3fold rotational symmetry about the axis of the peroxide ion, and the center of the O-O bond lies in the plane formed by the three neodymium atoms. The Nd-O bond lengths are 2.467 Å, and the O–O bond length is 1.512 Å. Each of the three neodymium atoms is coordinated to a single bis(2pyridinal)ethylenediimine ligand through its four nitrogen atoms, and the neodymium atoms are additionally bridged by a set of three chloride anions. Each neodymium atom is eightcoordinate. Identification of the peroxide anion as such (as opposed to other dioxygen species) was confirmed by X-ray crystallography and Fourier transform infrared (FT-IR) spectroscopy. The observed long O-O distance of 1.515(12) Å is consistent with previously reported values<sup>9,22</sup> In the FT-IR spectrum (Figure 2), the week band at 850  $cm^{-1}$ was attributed to the O–O bond vibration, which is consistent with previous reports.<sup>23</sup> Interestingly, this same band is absent in the Raman spectrum (Figure S4), where it is usually observed in most peroxide compounds. Selection rules would suggest that this peak should be weak or absent in IR but strong in Raman.

X-ray photoelectron spectroscopy (XPS) was conducted on the material, and the survey confirmed the presence of the expected elements (Figure S5). The anticipated differences



Figure 1. ORTEP diagram for  $[Nd_3Cl_6(L)_3(O)_2]Cl$ .



between the observed energies of peroxide oxygen atoms versus other dioxygen species are unfortunately minimal, so the

XPS data are of limited use in support of that assignment, especially relative to crystallographic and vibrational data.

In addition to the spectroscopic assignment of peroxide,  $[Nd_3Cl_6(L)_3(O)_2]Cl$  was tested for the peroxide species using Whatman starch iodide paper. The complex was dissolved in methanol, and then a small drop of solution was transferred onto a test strip and allowed to air-dry. A yellow color emerged on the test strip, indicating the presence of peroxide species within the complex.

A similar motif of neodymium atoms caging peroxide has appeared before in the work of Roitershtein.<sup>24</sup> However, our example has relatively longer Nd–O bonds and relatively shorter O–O bonds. Dysprosium and gadolinium complexes with hydroxo ions taking the place of the peroxide have also been reported.<sup>14,25</sup> These compounds have been of interest for their magnetic properties, so SQUID measurements were taken.

The magnetic susceptibility of the complex was measured over a temperature range from 5 to 300 K with a 1 T field, and these data are shown in Figure 3a. The measured magnetic



**Figure 3.** (a) Temperature-dependent magnetic susceptibility data at a magnetic field of 1 T from 300 to 5 K. Inset: Real component of ac susceptibility at 100 and 1000 Hz. (b) Isothermal magnetic-fielddependent susceptibility data at 5 K and up to 5 T. Inset: Langevin fitting results, where the red line is the fitting curve.

susceptibility shows a paramagnetic-like behavior, and the data in both zero-field-cooled and field-cooled conditions are completely overlapping with each other over the measured temperature range. This excludes the possibility of ferromagnetic or antiferromagnetic long-range orders in this system. However, at room temperature (300 K), the magnetic susceptibility is  $3 \times 10^{-4}$ , which is 2 orders magnitude larger than the typical paramagnetic materials. Therefore, we suggest the presence of superparamagnetism in this system because a complex with Nd<sup>3+</sup> ions could form small magnetic clusters without long-range order in this crystal structure, which has a large interatomic Nd<sup>3+</sup> distance and superexchange interaction of Nd<sup>3+</sup> ions via oxygen atoms and organic ligands seem infeasible.

To further prove that significant susceptibility is indeed coming from superparamagnetism rather than ferromagnetism (ferrimagnetism), an isothermal magnetic-field-dependent M-H curve was measured for this complex at 5 K and up to 5 T. The data are shown in Figure 3b. A clear nonlinear field-dependent M-H curve (at even very small magnetic fields) and the absence of hysteresis within the equipment resolution are observed and further rule out the existence of typical paramagnetism and ferromagnetism (ferrimagnetism) in this system. The relaxation moment is negligible down to 5 K over our consequential measurements, implying a blocking temperature far lower than 5 K. This is also consistent with the M-T measurement. For a superparamagnetic material, it is notable that hysteresis loss is negligible above the blocking temperature  $T_{\rm B}$ , i.e., a paramagnetic-like M-H behavior above  $T_{\rm B}$ .

The absence of hysteresis in the M-H curve further suggests that the blocking temperature  $T_{\rm B}$  is much lower than 5 K. Additional alternating-current (ac) susceptibility measurements are shown in the top-left inset of Figure 3b, where the real components of the magnetic susceptibility at two different frequencies (one at 100 Hz and another at 1000 Hz) are overlapping with each other under the ac magnetic field of an amplitude of 1000 Oe. This provides further clear evidence that  $T_{\rm B}$  is much lower than 5 K (the lowest temperature in the ac susceptibility measurements). Therefore, we can use the Langevin function with the temperature range above  $T_{\rm B}$  to quantitatively describe the M-H behavior at 5 K and calculate the associated cluster density and magnetic moment of the clusters in our compound.

The Langevin function used for our fitting is<sup>16</sup>

$$M(H, T) = n\mu L\left(\frac{\mu_0 H\mu}{k_{\rm B}T}\right) = n\mu \left[ \coth\left(\frac{\mu_0 H\mu}{k_{\rm B}T}\right) - \frac{k_{\rm B}T}{\mu_0 H\mu} \right]$$

where *n* is the cluster density,  $\mu_0$  is the magnetic permeability of vacuum,  $k_{\rm B}$  is the Boltzmann constant, and  $\mu$  is the magnetic moment of the cluster. The Langevin equation fits the M-Hcurve well, as seen in the inset in Figure 3b (the red line is the fitting curve), and further confirms the existence of superparamagnetism in this system. The fitting yields the magnetic moment of the cluster at 3.49  $\mu_{\rm B}$ , and the cluster density is 1.25  $\times 10^{21}$ /cm<sup>3</sup>. The magnetic moment of Nd<sup>3+</sup> is consistent with the free Nd<sup>3+</sup> ion moment (3.62  $\mu_{\rm B}$ ).<sup>26</sup> Additionally, the roomtemperature  $\chi T$  product is 66.05 cm<sup>3</sup>·K/mol, which is close to the theoretical value of the  $\chi T$  product of three free Nd<sup>3+</sup> ions (61.5 cm<sup>3</sup>·K/mol).

Superparamagnetism arises from an ensemble of noninteracting ferromagnets. The crystal structure of this complex has tight clusters of three neodymium atoms, with the clusters spaced widely apart. The most reasonable cause for the observed superparamagnetic behavior is that the clusters each behave ferromagnetically but are spaced too far apart to interact, thus leading to superparamagnetic behavior in the solid crystal material.

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We have shown that anion-templated assembly via atmospheric oxygen is a viable technique for the synthesis of large

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metal clusters when sufficiently oxophilic metals and oxygentolerant chemistry are used. Even if the chemistry is not moisture-tolerant, the complexes can still be easily reached without conventional air-and-water-free techniques by using the simple azeotropic distillation method, which excludes water well while still allowing the reaction to be exposed to atmospheric oxygen.

In addition, we have shown that such clusters may be of use because of their magnetic properties. For sufficiently large clusters with the metal centers localized toward the center, each cluster can act as a separate magnetic domain that flips easily and independently of nearby clusters. This produces superparamagnetic behavior on a much smaller scale than the more common approach of magnetic nanoparticles and still occurs even in a crystal. This may be of use in itself, or the implication of very small magnetic domains in similar materials may be of use for high-density data storage.

## ASSOCIATED CONTENT

## **③** Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c00234.

Additional crystallographic and spectroscopic information (PDF)

# **Accession Codes**

CCDC 1974941–1974943 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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### Notes

The authors declare no competing financial interest.

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# REFERENCES

(1) Hubin, T. J.; Busch, D. H. Template Routes to Interlocked Molecular Structures and Orderly Molecular Entanglements. *Coord. Chem. Rev.* **2000**, 200–202, 5–52.

(2) Vickers, M. S.; Beer, P. D. Anion Templated Assembly of Mechanically Interlocked Structures. *Chem. Soc. Rev.* 2007, 36, 211–225.

(3) Cram, D. J.; Kaneda, T.; Helgeson, R. C.; Lein, G. M. Spherands - Ligands Whose Binding of Cations Relieves Enforced Electron-Electron Repulsions. J. Am. Chem. Soc. **1979**, 101, 6752–6754.

(4) Hasenknopf, B.; Lehn, J.-M.; Boumediene, N.; Dupont-Gervais, A.; Van Dorsselaer, A.; Kneisel, B.; Fenske, D. Self-Assembly of Tetraand Hexanuclear Circular Helicates. *J. Am. Chem. Soc.* **1997**, *119*, 10956–10962.

(5) Sambrook, M. R.; Beer, P. D.; Wisner, J. A.; Paul, R. L.; Cowley, A. R. Anion-Templated Assembly of a [2]Catenane. J. Am. Chem. Soc. 2004, 126, 15364–15365.

(6) Metrangolo, P.; Pilati, T.; Terraneo, G.; Biella, S.; Resnati, G. Anion Coordination and Anion-Templated Assembly under Halogen Bonding Control. *CrystEngComm* **2009**, *11*, 1187–1196.

(7) Serpell, C. J.; Kilah, N. L.; Costa, P. J.; Félix, V.; Beer, P. D. Halogen Bond Anion Templated Assembly of an Imidazolium Pseudorotaxane. *Angew. Chem., Int. Ed.* **2010**, *49*, 5322–5326.

(8) Sambrook, M. R.; Beer, P. D.; Wisner, J. A.; Paul, R. L.; Cowley, A. R.; Szemes, F.; Drew, M. G. B. Anion-Templated Assembly of Pseudorotaxanes: Importance of Anion Template, Strength of Ion-Pair Thread Association, and Macrocycle Ring Size. *J. Am. Chem. Soc.* **2005**, *127*, 2292–2302.

(9) Gee, W. J.; MacLellan, J. G.; Forsyth, C. M.; Moubaraki, B.; Murray, K. S.; Andrews, P. C.; Junk, P. C. Caging Peroxide: Anion-Templated Synthesis and Characterization of a Rare-Earth Cluster. *Inorg. Chem.* **2012**, *51*, 8661–8663. (10) Andrews, P. C.; Beck, T.; Forsyth, C. M.; Fraser, B. H.; Junk, P. C.; Massi, M.; Roesky, P. W. Templated Assembly of a  $\mu$ 6-Co32-Dodecanuclear Lanthanum Dibenzoylmethanide Hydroxido Cluster with Concomitant Formation of Phenylglyoxylate. *Dalton Transactions* **2007**, 5651–5654.

(11) Natrajan, L.; Pécaut, J.; Mazzanti, M. Fixation of Atmospheric Co2 by a Dimeric Lanthanum Hydroxide Complex; Assembly of an Unusual Hexameric Carbonate. *Dalton Transactions* **2006**, 1002–1005.

(12) Guo, F.-S.; Chen, Y.-C.; Mao, L.-L.; Lin, W.-Q.; Leng, J.-D.; Tarasenko, R.; Orendáč, M.; Prokleška, J.; Sechovský, V.; Tong, M.-L. Anion-Templated Assembly and Magnetocaloric Properties of a Nanoscale {Gd38} Cage Versus a {Gd48} Barrel. *Chem. - Eur. J.* **2013**, *19*, 14876–14885.

(13) Miró, P.; Pierrefixe, S.; Gicquel, M.; Gil, A.; Bo, C. On the Origin of the Cation Templated Self-Assembly of Uranyl-Peroxide Nanoclusters. *J. Am. Chem. Soc.* **2010**, *132*, 17787–17794.

(14) Tang, J.; Hewitt, I.; Madhu, N. T.; Chastanet, G.; Wernsdorfer, W.; Anson, C. E.; Benelli, C.; Sessoli, R.; Powell, A. K. Dysprosium Triangles Showing Single-Molecule Magnet Behavior of Thermally Excited Spin States. *Angew. Chem., Int. Ed.* **2006**, *45*, 1729–1733.

(15) Woodruff, D. N.; Winpenny, R. E. P.; Layfield, R. A. Lanthanide Single-Molecule Magnets. *Chem. Rev.* 2013, 113, 5110–5148.

(16) Bean, C. P.; Livingston, J. D. Superparamagnetism. J. Appl. Phys. **1959**, 30, S120-S129.

(17) Iovu, M.; Maithufi, N.; Mapolie, S. Copper-Mediated Atrp of Methyl Methacrylate in Polar Solvents Using a Bifunctional Pyridinal Diimine Ligand. *Macromol. Symp.* **2003**, *193*, 209–226.

(18) Abdoh, M.; Warad, I.; Naveen, S.; Lokanath, N. K.; Salghi, R. Crystal Structure of (1e,1'e)-N,N'-(Ethane-1,2-Diyl)Bis[(Pyridin-2-Y1)Methanimine]. Acta Crystallographica Section E 2015, 71, No. 0431.

(19) El-Qisairi, A.; Qaseer, H.; Alshahateet, S.; Qaseer, M.-K.; Zaghal, M.; Al-Btoush, W. E.; Dawe, L. Supramolecular Interactions Involved in the Solid State Structure of N,N'-[Bis(Pyridin-2-Y1)Formylidene]Ethane-1,2-Diamine. *Croat. Chem. Acta* **2014**, *87*, 123–128.

(20) Sheldrick, G. Shelxt - Integrated Space-Group and Crystal-Structure Determination. *Acta Crystallogr., Sect. A: Found. Adv.* 2015, 71, 3–8.

(21) Sheldrick, G. Crystal Structure Refinement with Shelxl. Acta Crystallogr., Sect. C 2015, 71, 3–8.

(22) Coles, M. P.; Hitchcock, P. B.; Khvostov, A. V.; Lappert, M. F.; Li, Z.; Protchenko, A. V. Crystalline Amidocerium(Iv) Oxides and a Side-on Bridging Dioxygen Complex. *Dalton Transactions* **2010**, *39*, 6780–6788.

(23) Patroniak, V.; Kubicki, M.; Radecka-Paryzek, W. The First Example of M-H2:H2-Peroxo-Bridged Macrocyclic Lanthanide Complex. The Crystal Structure of [Lu2{Me2pyo[16]Trienen\$}2-(M-H2:H2-O2)Cl2](Clo4)2 Dioxane Solvate. J. Inclusion Phenom. Mol. Recognit. Chem. 2004, 49, 121–125.

(24) Roitershtein, D. M.; Vinogradov, A. A.; Lyssenko, K. A.; Nifant'ev, I. E. Self-Assembly of Heteroleptic Tetranuclear Carboxylate Complexes of Yttrium and Lanthanides During Hydrolysis and Oxidation of Rare Earth Homoleptic Carboxylates. *Inorg. Chem. Commun.* **2017**, *84*, 225–228.

(25) Fujimori, I.; Mita, T.; Maki, K.; Shiro, M.; Sato, A.; Furusho, S.; Kanai, M.; Shibasaki, M. Key Role of the Lewis Base Position in Asymmetric Bifunctional Catalysis: Design and Evaluation of a New Ligand for Chiral Polymetallic Catalysts. *J. Am. Chem. Soc.* **2006**, *128*, 16438–16439.

(26) Lide, D. R. CRC Handbook of Chemistry and Physics, Internet version 2005; CRC Press: Boca Raton, FL, 2005; pp 4–116.