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Anion-dependent assembly of Dy complexes: structures and magnetic behaviors

Peng Chen,*a,b Meiqi Zhang,² Wenbin Sun,³ Hongfeng Li,³ Lang Zhao³ and Pengfei Yan*³

Self-assembly of 2-aldehyde-8-hydroxyquinoline, histamine dichloride and LnX₃·6H₂O (X⁻ = OAc⁻, NO₃⁻ and ClO₄⁻) affords a series of lanthanide complexes Nd₃(nma)₂(OAc)₃·3CH₃OH·0.5H₂O (1a), Ln₃(nma)₂(OAc)₃·2CH₃OH [Ln = Tb (1b) and Dy (1c)], [Ln(nma)(NO₃)₃(DMSO)]·CH₃OH [Ln = Nd (2a), Tb (2b), Dy (2c) and Er (2d)] and [Dy(nma)₂]ClO₄·0.5CH₃OH (3) (Hnma = N-(2-(8-hydroxyquinolinyl)methane(2-(4-imidazolyl)ethanamine)). It is noted that the formation and structures of 1–3 are anion-dependent, where diverse coordination modes are detected for acetates in trinuclear 1 as compared to single coordination mode for nitrates in mononuclear 2. In the case of 3, the Dy³⁺ ion is completely encapsulated by two ligands with uncoordinated perchlorate anion balancing the charge. Magnetic measurement shows that the Dy complexes of 1c, 2c and 3 exhibit slow relaxations under zero dc field. It is noted that single molecular magnet behavior is obtained for 2c and 3 under an applied dc field of 2000 Oe.

Scheme 1. The molecular structure of the ligand Hnma.

Meanwhile, great efforts have been devoted to the crystal engineering for the fabrication of functional materials, on account of the significant contribution of the structures and compositions to the potential properties. The synthesis is often complicated due to the versatile coordination geometries of the lanthanide ions, and the structural diversity is accompanied with a variety of factors such as ionic radius, the nature of the counter ions, the structure of the ligand and so on. The importance of the anions in the self-assembly is less noted, although they can tune the structures through their diversified coordination modes. Recent example has demonstrated the importance of Cl⁻ anions in the self-assembly of 24-metal and 32-metal complex that offers an opportunity to study the formation of high-nuclearity clusters in NIR property. We herein present the syntheses, structures and characterization of a series of lanthanide complexes [Nd₃(nma)₂(OAc)₃]·3CH₃OH·0.5H₂O (1a), [Ln₃(nma)₂(OAc)₃]·2CH₃OH [Ln = Tb (1b) and Dy (1c)], [Ln(nma)(NO₃)₃(DMSO)]·CH₃OH [Ln = Nd (2a), Tb (2b), Dy (2c) and Er (2d)] and [Dy(nma)₂]ClO₄·0.5CH₃OH (3), which...
are obtained from the in-situ condensation of LnX₅·6H₂O (X= 0Ac, NO₃, ClO₄), aq and histamine. The result highlights significant role of the anions with distinct coordination modes in the assembly of 1–3 that three distinct species complexes have been prepared under the similar condition. Magnetic measurement shows that 1c, 2c and 3 exhibit slow relaxations of the magnetization.

**Experimental section**

**Materials and Measurements**

The commercially available chemicals were analytical reagent grade and used without further purification. 2-Aldehyde-8-hydroxyquinoline (aq) was synthesized according to the reported methods. The ligand N-(2-(8-hydroxyquinolinyl)methane(2-(4-imidazolyl)ethanamine) (Hmna) was in-situ formed by the condensation of ahq and histamine in the reaction system (Scheme 1). Elemental analyses were performed on an Elementar Vario EL cube analyzer. FT-IR spectra were obtained on a Perkin-Elmer Spectrum One spectrophotometer by using KBr disks in the range of 4000–370 cm⁻¹. The magnetic susceptibility measurements were obtained using a Quantum Design SQUID magnetometer MPMS-3 operating between 2 and 300 K for dc−applied fields ranging from −7 to 7 T, ac susceptibility measurements were carried out under an oscillating ac field of 2 °C/min under air atmosphere in the temperature range of 25–780 °C. All measurements were carried out by using fresh crystals.

Single crystals of 1–3 were selected for X-ray diffraction analysis on a Xcalibur, Eos diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The crystals were kept under N₂ atmosphere at 150 K for 1 and 293K for 2 and 3 during data collection. The structures were solved by the direct methods and refined on F² by full-matrix least-square using the SHELXTL-97 program. The Ln⁺ ions were firstly located, and then non-hydrogen atoms (C, N, O, S and Cl) were placed from the subsequent Fourier-difference maps and refined anisotropically. The H atoms were introduced in the calculated positions and refined with fixed geometry with respect to their carrier atoms. Large residual Fourier peaks and holes near the metal ions in 1a–1c were detected, which would be probably owing to the accounted twinning. The absorption correction had been tried times, but it had not improved. In 1a–1c, the diffused electron densities resulting from the residual solvents were removed from the dataset by using the SQUEEZE routine of PLATON and it was further refined using the data generated. With respects to the TG analyses and the solvents added, it was supposed two more (1a) and eight (1b) and 1c) methanol molecules were included, respectively, which had been added in the unit cell contents. The crystallographic formulae (1a–1c) have been modified to include non-located atoms. More details concerned with constraints and the refinements had been supplied in the cif files. The experimental details for the structural determination are presented in Table 1.

**Synthesis of 1–3**

[Nd(mma)(OAc)₂·3CH₃OH·0.5H₂O (1a)]

Self-assembly reactions of ahq, histamine dihydrochloride, triethylamine and Ln(OAc)₃·6H₂O (Ln= Nd (1a), Tb (1b), Dy (1c)) afforded the corresponding complexes 1a–1c, respectively (Scheme 2). For the case of 1a: 0.129 g (0.3 mmol) Nd(OAc)₃·6H₂O, 0.017 g (0.1 mmol) ahq, 0.018 g (0.1 mmol) histamine dihydrochloride and 0.010 g (0.1 mmol) triethylamine were dissolved in a mixture of CH₃OH/CH₂Cl₂ (5/10 ml, v/v). Then diethyl ether was allowed to diffuse slowly into the filtrate. Crystals of 1a suitable for single crystal X-ray analysis could be obtained in 9 days. Anal. Calc for C₂₇H₆₆NdO₁ₙ₂O₁₉.1₅ (1481.75): C, 38.10; H, 4.01; N, 7.56 wt%. Found: C, 38.14; H, 4.03; N, 7.59 wt%. IR (KBr, cm⁻¹): 3386, 3158, 2915, 1547, 1449, 1104, 1019, 845, 765, 670.

[Tb(mma)(OAc)₂·2CH₃OH (1b)]

Anal. Calc for C₂₉H₆₆NdO₁₉.1₅Tb (1484.72): C, 37.21; H, 3.73; N, 7.55 wt%. Found: C, 37.29; H, 3.85; N, 7.50 wt%. IR (KBr, cm⁻¹): 3380, 3103, 2920, 1556, 1456, 1106, 1104, 845, 766, 672.

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[Nd(nma)(NO₃)]·2CH₃OH (1c)

Anal. Calcd for CₓHᵧNₒDₜOₛ (1495.48): C, 36.94; H, 3.71; N, 7.49 wt%. Found: C, 37.02; H, 3.81; N, 7.43 wt%. IR (KBr, cm⁻¹): 3394, 3114, 2925, 1558, 1456, 1107, 1018, 837, 767, 673.

[Nd(NO₃)₂(DMSO)]·CH₃OH (2a)

2a-2d were prepared as above starting from Ln(NO₃)₃·6H₂O [Ln = Nd (2a), Tb (2b), Dy (2c) and Er (2d)]. For the case of 2a, Nd(NO₃)₃·6H₂O 0.088 g (0.2 mmol), 0.034 g (0.2 mmol) ahq, 0.036 g (0.2 mmol) histamine dihydrochloride and 0.020 g (0.2 mmol) triethylamine were dissolved in a mixture of CH₃OH/CH₃Cl/DMSO (2/5/1 ml, v/v/v). Then diethyl ether was allowed to diffuse slowly into the filtrate. Crystals suitable for single crystal X-ray analysis could be obtained in 6 days. Anal. Calcd for CₓHᵧNₒDₜOₛ: C, 30.5; H, 3.71; N, 7.49 wt%. IR (KBr, cm⁻¹): 3316, 3142, 3019, 2909, 1636, 1593, 1457, 1385, 1285, 1105, 1006, 843, 735.

[Tb(nma)(NO₃)]·2CH₃OH (2b)

Anal. Calcd for CₓHᵧNₒDₜOₛ (643.72): C, 33.59; H, 3.60; N, 13.06; S, 4.98 wt%. Found: C, 33.59; H, 3.61; N, 13.06; S, 4.98 wt%. IR (KBr, cm⁻¹): 3316, 3142, 3019, 2909, 1636, 1593, 1457, 1385, 1285, 1105, 1006, 843, 735.

[Dy(nma)(NO₃)₂(DMSO)]·CH₃OH (2c)

Anal. Calcd for CₓHᵧNₒDₜOₛ (661.98): C, 32.66; H, 3.50; N, 12.70; S, 4.85 wt%. Found: C, 32.68; H, 3.49; N, 12.70; S, 4.85 wt%. IR (KBr, cm⁻¹): 3311, 3140, 3024, 2914, 1637, 1598, 1459, 1381, 1308, 1108, 846, 738.

[Er(nma)(NO₃)₂(DMSO)]·CH₃OH (2d)

Anal. Calcd for CₓHᵧNₒDₜOₛ (666.75): C, 32.43; H, 3.48; N, 12.60; S, 4.81 wt%. Found: C, 32.45; H, 3.49; N, 12.60; S, 4.79 wt%. IR (KBr, cm⁻¹): 3311, 3113, 3026, 2912, 1639, 1596, 1461, 1384, 1306, 1106, 1008, 842, 743.

[Dy(nma)]·ClO₄·0.5CH₃OH (3)

0.057 g (0.1 mmol) Dy(ClO₄)·6H₂O, 0.034 g (0.2 mmol) ahq, 0.036 g (0.2 mmol) histamine dihydrochloride and 0.020 g (0.2 mmol) triethylamine were dissolved in CH₃OH solution (5 ml). Then diethyl ether was allowed to diffuse slowly into the filtrate. Crystals suitable for single crystal X-ray analysis could be obtained in 6 days. Anal. Calcd for CₓHᵧNₒDₜOₛO₅ (808.56): C, 45.31; H, 3.49; N, 13.86 wt%. Found: C, 45.29; H, 3.48; N, 13.84 wt%. IR (KBr, cm⁻¹): 3395, 3011, 2921, 1631, 1591, 1457, 1337, 1106, 838, 764, 622.

Scheme 2. The synthetic routes of 1–3.

Results and Discussion

Structural description of 1–3

Single crystal X-ray diffraction analysis reveals that 1a–1c are isoostructural and crystallize in the triclinic space group PT. Therefore, a full description of 1c is given as a representative example. In the asymmetric unit of 1c, there are two crystallographically independent [Dy(nma)](OAc)(-) units, which adopt nearly linear arrangements (Figure 1). Dy1, Dy2 and Dy3 ions possess the similar coordination environments to Dy4, Dy5 and Dy6 ions, respectively, so the moiety containing Dy1 ion are selected to describe the structural feature. Dy1 ion is nine-coordinated to one O and three N atoms of the ligand and five O atoms from the acetate groups. Dy2 ion is nine-connected to seven O atoms from the acetate groups, and two O atoms of the ligand. Dy3 ion is nine-ligated to one O and three N atoms of the ligand, and five O atoms from the acetate groups as well. The Dy–O(N) bond lengths are in the range of 2.288(13)–2.570(10) Å in accordance with the reported values. The Nᵥmin atoms are exclusively kept connected to the Dy ions, while the Nᵥmax atoms remain uncoordinated in contrast. The Dy1···Dy2 and Dy2···Dy3 distances of 3.6700(7) and 3.7991(8) Å are similar to that of Dy4···Dy5 and Dy5···Dy6 (3.6539(8) and 3.8562(8) Å), which are compatible to those in the Ln₃ triangles. Various coordination modes have been detected for acetate groups in 1c, which act as a bridge between the terminal and central Dy³⁺ ions in addition to the phenoxido bridges. Dy1 and Dy2 ions share two acetate groups in the chelating-bridging mode, and Dy2 and Dy3 ions share as well two acetate groups in the chelating-bridging and bridging modes, respectively. The intermolecular N–H···O H-bonds are found among the two crystallographically distinct units, while π–π interactions could be observed among the quinolinyl groups (Figure 2). It is noted that only chelating and chelating bridging coordination modes are detected in 1a, although the Nd···Nd distances are in the similar range of 3.7855(8)–3.8331(8) Å.
Referring to the ligand, the two crystallographically distinct nitrate groups axially chelate Dy ion and the DMSO molecule is horizontally attached to the Dy ion. The Dy–O(N) distances are in the range of 2.314(3)–2.563(3) Å, whilst the distances of Dy–O (phenolate and sulfoxide O atoms) are significantly shorter. The π–π interactions could be detected with the overlap of the quinolinyl groups of the two adjacent crystallographically equivalent [Dy(nma)]\(^{3+}\) units, while the π–π interactions between two adjacent crystallographically equivalent [Dy(nma)]\(^{3+}\) units is arisen from the overlap of imidazolyl and quinolinyl groups. Furthermore, the two crystallographically distinct units form π–π interactions as well. The intermolecular H-bonds with N–H···O distances of 2.703(5) and 2.773(5) Å are observed among the crystallographically equivalent units, whilst H-bonds with N–H···O distances of 2.935(5) and 3.023(6) Å among the perchlorate and imidazolyl groups.

Similar results could be obtained with equivalent NaOH instead of triethylamine for 1–3, while all attempts to synthesize complexes incorporated with chlorides were unsuccessful. Initially, the attempt for 2 were prepared by using a solution of CH\(_2\)OH/CH\(_2\)Cl\(_2\), where precipitates formed and only small crystals were found in very low yield. We therefore adjust the synthetic condition to improve the solubility through the addition of a few DMSO into the reaction mixture. As expected, the reaction solution tuned to clear and large crystals in high yield were collected. The stoichiometry and structures of these complexes are dependent on the nature of the anion, and the presence of different anions OAc\(^{−}\), NO\(_3\)\(^{−}\) and ClO\(_4\)\(^{−}\) provided by the lanthanide salts has made significant contribution to the formation of diversified structures of 1–3. The successful preparation of trinuclear 1 is attributed to the variable coordination modes of the acetate anions to the lanthanide ions, while nitrate groups are bound to the Ln\(^{3+}\) ions in the chelating mode as a terminal in 2. And mononuclear 3 encapsulated by two ligands is obtained by the introduction of uncoordinated perchlorate. The anions in versatile coordination modes would facilitate the formation of multinuclear complexes.

![Figure 2](image1.png)

**Figure 2.** Views showing the intermolecular H-bonding (a) and π–π interactions (b) in 1c. (Hydrogen atoms have been omitted for clarity; symmetry codes: #1: x, y-1, z; #2: x+1, y, z; #3: 2-x, 2-y, -z; #4: 1-x, 1-y, 1-z)

![Figure 3](image2.png)

**Figure 3.** Partially labeled crystal structure and a view showing the intermolecular H-bonding and π–π interactions in 2c. (Hydrogen atoms have been omitted for clarity; symmetry codes: #1:2-x, -y, -z; #2: x, y-1, z-1)

X-ray crystallographic analysis reveals that 3 crystallizes in the monoclinic space group P2\(_1\)/c. In the asymmetric unit of 3, there are two crystallographically distinct [Dy(nma)]\(^{3+}\) units, one methanol molecule and two perchlorate groups (Figure 4). Each Dy\(^{3+}\) ion encapsulated by two ligands is eight-coordinated to two O atoms and six N atoms, adopting a biaugmented trigonal prism arrangement. The Dy–O distances are in the range of 2.260(3)–2.300(3) Å and Dy–N distances are in the range of 2.464(4)–2.631(4) Å. The π–π interactions could be detected with the overlap of the quinolinyl groups of the two adjacent crystallographically equivalent [Dy1(nma)]\(^{3+}\) units, while the π–π interactions between two adjacent crystallographically equivalent [Dy1(nma)]\(^{3+}\) units is arisen from the overlap of imidazolyl and quinolinyl groups. Furthermore, the two crystallographically distinct units form π–π interactions as well. The intermolecular H-bonds with N–H···O distances of 2.703(5) and 2.773(5) Å are observed among the crystallographically equivalent units, whilst H-bonds with N–H···O distances of 2.935(5) and 3.023(6) Å among the perchlorate and imidazolyl groups.

![Figure 4](image3.png)

**Figure 4.** Partially labeled crystal structure of 3 and the π–π interactions (a), and intermolecular H-bonding among Dy1 and Dy2 units (b). Views showing the intermolecular H-bonding and π–π interactions among the crystallographically equivalent Dy1 units (c) and Dy2 units (d), respectively. (Hydrogen atoms have been omitted for clarity; symmetry codes: #1: 1-x, -0.5+y, 0.5-z; #2: x, 1.5-y, 0.5+z; #3: 1-x, 1-y, 1-z; #4: -x, -0.5+y, 0.5-z; #5: x, 1.5-y, z-0.5; #6: -x, 1-y, -0.5+z; #7: 1-x, 0.5+y, 0.5-z; #8: 1+x, 1.5-y, -0.5+z)

**Magnetic properties of 1c, 2c and 3**

The direct-current (dc) magnetic measurements are performed in an applied magnetic field of 1000 Oe (Figure 5) for 1c, 2c and 3 in the temperature range of 2–300 K. At the
room temperature, the values of $\chi T$ are 82.94, 14.09 and 14.14 cm$^3$ K mol$^{-1}$ for complexes 1c, 2c and 3, respectively, which are close to the expected value for six, one and two independent Dy$^{3+}$ ions (1c: 85.02, 2c: 14.17, 3: 14.17 cm$^3$ K mol$^{-1}$): Dy$^{3+}$ (S = 5/2, L = 5, $g$ = 4/3, C = 14.17 cm$^3$ K mol$^{-1}$). For 1c, the $\chi T$ product remained constant down to 75 K on lowering the temperature before dropping rapidly down to 40.96 cm$^3$ K mol$^{-1}$ at 2 K. The decrease of $\chi T$ at low temperature obviously suggests the presence of intramolecular antiferromagnetic interactions within Dy$^{3+}$ ions. Similar results can be observed for complexes 2c and 3. The $\chi T$ products gradually decrease on lowering the temperature and drop to minimum values of 9.98 and 11.62 cm$^3$ K mol$^{-1}$ at 2 K. The gradual decrease before 75 K is due to the thermal depopulation of the Stark sublevels, whereas the latter rapid drop may be ascribed to the weak antiferromagnetic interactions between the lanthanide centers, even if magnetic anisotropy might also partially affect low temperature susceptibility.

**Figure 5.** Temperature dependence of the $\chi T$ products at 1000 Oe.

**Figure 6.** The frequency dependence of the out-of-phase ac susceptibility of 2c at the indicated temperature under an applied dc field of 2000 Oe.

**Figure 7.** The frequency dependence of the out-of-phase ac susceptibility of 3 at the indicated temperature under an applied dc field of 2000 Oe.

Magnetization ($M$) data for 1c, 2c and 3 are collected in the 0-7 T field range below 5K. For 1c, 2c and 3, the magnetization versus $H/T$ data at different temperatures show nonsuperposition plots, and a gradual increase of the magnetization at high fields, without a saturation even at 7 T, revealing the presence of a significant magnetic anisotropy and/or low-lying excited states. The dynamics of the magnetization for 1c, 2c and 3 are investigated using alternating current susceptibility measurements. A temperature dependent increase of the in-phase signal, together with the appearance of an out-of-phase signal is observed for 1c, 2c and 3 (Figure S16–18). It reveals the onset of slow magnetization relaxation, which is typical for SMM properties. Although the ac susceptibility as a function of the temperature does not show any peak in the out-of-phase ac susceptibility in zero dc field, it is affected by the dc field. The fast quantum tunneling of magnetization is slowed down by the applied field that the peak of the out-of-phase ac susceptibility is observed under a 2000 Oe dc filed for 2c and 3, as shown in Figure S20–21.

To further probe the dynamics of 1c, 2c and 3, ac susceptibility measurements as a function of the frequency at different temperatures under a 2000 Oe dc field are carried out (Figure 6–7). The data plotted as Cole-Cole plots of 2c in the temperature range of 3–9.5 K shows a relatively symmetrical shape and can be fitted to the generalized Debye model,\textsuperscript{23} with $\alpha$ parameters in the range of 0.03–0.21. The relaxation time is extracted from the frequency-dependent data between 2–11 K and the Arrhenius plot obtained from these data is given in Figure 7. Above 7.5 K, the relaxation follows a thermally activated Orbach mechanism with an energy gap of 67 K and a preexponential factor $\tau_0$ of 1.68×10$^{-7}$ s based on the Arrhenius law [$\tau = \tau_0 \exp(U_{\text{eff}}/K_B T)$]. Meanwhile, the occurrence of two distinct peaks for the out-of-phase ac signals ($\chi''$) is evident at higher frequencies, revealing the possibility of a multiple relaxation process.\textsuperscript{24} The Cole-Cole plots of 3 in the temperature range of 2–12 K exhibits a unique double-ridge structure as well. The anisotropic energy gaps are calculated to be 16 K (1.0×10$^{-5}$ s) and 47 K (4.6×10$^{-6}$ s) for the low temperature and high temperature domains, respectively. It is noted that the $\tau_0$ values are larger than the expected values for SMM,\textsuperscript{25} which is probably enhanced by the presence of QTM. The deviation below 7 K from Arrhenius behavior is owing to the replacement of thermally activated spin reversal by the direct process. The magnetic slow-relaxation behavior of 2c and 3 is arisen from the presence of anisotropic Dy$^{3+}$ ions. For 1c, the weak signals after applying dc field show unconspicuous slow magnetic relaxation behaviour. It is possibly due to the relative close distance between Dy$^{3+}$ ions that the weak intramolecular magnetic coupling shortcuts the thermally activated relaxations.

**Conclusion**

In summary, we have successfully synthesized three species of eight mma-based lanthanide complexes with acetate, nitrate, and perchlorate as the counter ions, respectively, where the ligand is in-situ generated during the reaction. Structural analysis reveals the importance of the anions in different geometries for the self-assembly and the stoichiometry. The connection of acetate groups to the Ln$^{3+}$ ions through three coordination modes gives rise to the formation of trinuclear 1, whilst mononuclear 2 is derived from nitrates in a single chelating mode. In the presence of uncoordinated perchlorate, the Dy is completely encapsulated by two ligands in contrast to
the cases of 1 and 2. The complexes 1–3 would contribute to understand the crucial role of the anions in the assembly of the supramolecular architectures. The magnetic results of 1–3 highlight the possibility to tune the dynamic behavior through the adjustment on the structural environment. 2-aldehyde-8-hydroxyquinoline-based ligand would be potentially utilized for the construction of SMMs.

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Notes and references


The *in-situ* reaction of 2-aldehyde-8-hydroxyquinoline, histamine and LnX₃·6H₂O (X⁻ = OAc⁻, NO₃⁻ and ClO₄⁻) affords three distinct species of eight lanthanide complexes.