

Two Hydroxo Bridged Dinuclear Lanthanide Phen Complexes: $[\text{Ln}_2(\text{phen})_4(\text{H}_2\text{O})_4(\text{OH})_2](\text{phen})_2(\text{NO}_3)_4$ with Ln = Tm, Yb

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Lanthanide, Dinuclear Complexes, π - π Stacking Interactions

Two isostructural hydroxo bridged dinuclear lanthanide phen complexes of general composition $[\text{Ln}_2(\text{phen})_4(\text{H}_2\text{O})_4(\text{OH})_2](\text{phen})_2(\text{NO}_3)_4$ with Ln = Tm (1), Yb (2) were prepared by reactions of the corresponding lanthanide nitrate and phenanthroline monohydrate in $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ at pH = 5.5. They crystallize in the triclinic space group $P\bar{1}$ (no. 2) with the cell dimensions: $a = 11.233(1)$, $b = 11.456(1)$, $c = 14.011(2)$ Å, $\alpha = 93.91(1)^\circ$, $\beta = 98.20(1)^\circ$, $\gamma = 108.21(1)^\circ$, $V = 1683.0(3)$ Å³, $Z = 1$ for 1 and $a = 11.236(1)$, $b = 11.480(2)$, $c = 13.986(2)$ Å, $\alpha = 93.91(1)^\circ$, $\beta = 98.17(1)^\circ$, $\gamma = 108.33(1)^\circ$, $V = 1682.9(3)$ Å³, $Z = 1$ for 2. The crystal structures are composed of the hydroxo bridged dinuclear $[\text{Ln}_2(\text{phen})_4(\text{H}_2\text{O})_4(\text{OH})_4]^{4+}$ complex cations, hydrogen bonded NO_3^- anions and π - π stacking $(\text{phen})_2$ dimers. The lanthanide atoms are each surrounded by two phen ligands, two H_2O molecules and two μ -OH groups to complete a tetragonal antiprismatic LnN_4O_4 coordination. Via two common μ -OH groups, two neighboring tetragonal antiprisms are condensed to form a centrosymmetric dinuclear $[\text{Ln}_2(\text{phen})_4(\text{H}_2\text{O})_4(\text{OH})_4]^{4+}$ complex cation. The complex cations and $(\text{phen})_2$ dimers are assembled via π - π stacking interactions and hydrogen bondings into 2D layers parallel to $(10\bar{1})$, between which the hydrogen bonded NO_3^- anions are sandwiched. The Tm compound shows paramagnetic behavior with an experimental magnetic moment of $7.51 \mu_B$ at room temperature. No magnetic ordering is evident down to 5 K. Over the temperature range 70 - 300 K, the Yb compound obeys the Curie-Weiss law with an experimental magnetic moment of $4.32 \mu_B$ at room temperature and shows weak ferrimagnetic behavior at low temperature.

Introduction

About ten years ago, Rybakov and coworkers first reported a Gd phen nitrate compound built up by mononuclear $[\text{Gd}(\text{phen})_2(\text{NO}_3)_3]$ complex molecules [1], and later, two research groups respectively obtained $\text{La}(\text{phen})_2(\text{NO}_3)_3$ [2] and $\text{Lu}(\text{phen})_2(\text{NO}_3)_3$ [3]. Structural characterizations showed that the La and Lu complexes are isostructural with the Gd compound. However, our previous investigation led to the serendipitous formation of a lanthanum complex with the formula $[\text{La}(\text{phen})_2(\text{H}_2\text{O})_2(\text{NO}_3)_2](\text{NO}_3)(\text{phen})_2(\text{H}_2\text{O})$, which is composed of monovalent $[\text{La}(\text{phen})_2(\text{H}_2\text{O})_2(\text{NO}_3)_2]$ complex cations, hydrogen bonded nitrate anions, H_2O molecules and uncoordinating phen molecules [4]. The La(III) complex cations could be viewed as resulting from replacement of one co-

ordinating nitrate group of the $[\text{La}(\text{phen})_2(\text{NO}_3)_3]$ unit by a water molecule. Such findings inspired further systematic investigations on the seemingly simple phen / lanthanide nitrate system. The reactions of lanthanide nitrate and phen in mixed solvents of CH_3OH and H_2O produced a series of lanthanide(III) mixed ligand complexes, which could be grouped into three classes (i) $[\text{Ln}(\text{phen})_2(\text{H}_2\text{O})_2(\text{NO}_3)_2]$ with Ln = Pr, Nd, Sm, Eu, Tb, Dy [5, 6], (ii) $[\text{Ln}(\text{phen})_2(\text{H}_2\text{O})_2(\text{NO}_3)_2](\text{NO}_3)(\text{phen})_2(\text{H}_2\text{O})$ with Ln = La, Ce [4, 7] and (iii) $[\text{Ln}_2(\text{phen})_4(\text{H}_2\text{O})_4(\text{OH})_2](\text{phen})_2(\text{NO}_3)_4$ with Ln = Er, Lu [8]. Different from the first and second classes, the third class compounds feature hydroxo bridged tetravalent dinuclear complex cations. In order to ascertain the possible interactions between the metal atoms within the dinuclear cations, we continued our work to span the series between Er and Lu, which gave

Table 1. Crystal and refinement data for 1 and 2.

Compounds	1	2
Formula; mole mass	C ₇₂ H ₅₈ N ₁₆ O ₁₈ Tm ₂ ; 1773.20 amu	C ₇₂ H ₅₈ N ₁₆ O ₁₈ Yb ₂ ; 1781.42 amu
Crystal shape	colorless plate	colorless plate
Crystal size	0.53 × 0.17 × 0.09 mm	0.67 × 0.27 × 0.11 mm
Space group, formula units	<i>P</i> $\bar{1}$ (no. 2), 1	<i>P</i> $\bar{1}$ (no. 2), 1
Unit cell dimensions	<i>a</i> = 11.233(1) Å, <i>b</i> = 11.456(1) Å, <i>c</i> = 14.011(2) Å α = 93.91(1)°, β = 98.20(1)°, γ = 108.21(1)°	<i>a</i> = 11.236(1) Å, <i>b</i> = 11.480(2) Å, <i>c</i> = 13.986(2) Å α = 93.91(1)°, β = 98.17(1)°, γ = 108.33(1)°
<i>V</i> ; <i>D</i> _x	1683.0(3) Å ³ ; 1.750 g cm ⁻³	1682.9(3) Å ³ ; 1.758 g cm ⁻³
Measurement	Bruker P4 four-circle diffractometer, Mo- <i>K</i> _α radiation (λ = 0.71073 Å); $\vartheta/2\vartheta$ scan mode, 2° ≤ 2 ϑ ≤ 55°	
Structure refinement	empirical absorption correction (ψ -scan method); direct methods, difference Fourier syntheses; full-matrix least-squares refinement, $w = [\sigma^2(F_o^2) + (qP)^2 + rP]^{-1}$ with $P = (F_o^2 + 2F_c^2)/3$, Shelxl-97 [10]	
<i>q</i> ; <i>r</i>	0.0916; 16.0029	0.1375; 3.823
μ ; Transmission	2.707 (mm ⁻¹); 0.495-0.808	2.850 (mm ⁻¹); 0.634-0.815
Extinction coefficient	0.0036(8)	
<i>N</i> (parameter)	491	489
<i>N</i> (<i>hkl</i>) (meas./unique)	8922/7736	8899/7715
<i>N</i> (<i>hkl</i>)(<i>I</i> > 2 σ (<i>I</i>))	6527	7033
<i>R</i> ₁ ; <i>wR</i> ₂ ^a	0.0547; 0.1386	0.0452; 0.1343
Goodness of fit on <i>F</i> ²	1.099	1.072
$\delta\rho_{\min}$; $\delta\rho_{\max}$	-3.794; 2.024 [e. Å ⁻³]	-2.930; 2.649 [e. Å ⁻³]

$$^a wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$$

rise to successful syntheses of the title compounds in high yields. Herein, we report their structural and magnetic characterizations.

Experimental Section

Physical measurements

All chemicals of p.a. grade were purchased from Shanghai Chemicals Company and used without further purification. The C, H and N microanalyses were performed with a Heraeus Rapid-CHNO elemental analyzer. The magnetic susceptibility measurements on polycrystalline samples of 1 and 2 were carried out in the temperature range 5 ≤ *T* (K) ≤ 300 with a SQUID magnetometer (Quantum Design Model MPMS-7) operating at 10000G. Diamagnetic corrections of the constituent atoms were estimated from Pascal's constants as $\chi_{\text{dia.}} = -480 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ [9].

Preparation

[Tm₂(phen)₄(H₂O)₄(OH)₂](phen)₂(NO₃)₄ (1): A solution obtained by dissolving 0.142 g (1.00 mmol) Tm₂O₃ in 4 ml (65%) HNO₃ was evaporated to dryness and 25 ml CH₃OH/H₂O (1:1 v/v) was added. The mixture was stirred until complete dissolution. To the stirred solution was added 0.594 g (3.00 mmol) phenanthroline monohydrate. The colorless solution (pH = 5.5) was then

heated to boiling. The orange solution was finally allowed to stand at room temperature. After 5 d, plate-like colorless crystals were formed. Yield: ca. 73% on the basis of the initial Tm₂O₃ input. C₇₂H₅₈N₁₆O₁₈Tm₂ (%): calcd. C 48.77, H 3.30, N 12.64; found C 48.53, H 3.47, N 12.35.

[Yb₂(phen)₄(H₂O)₄(OH)₂](phen)₂(NO₃)₄ (2): 2 was analogously prepared except for 0.197 g (1.00 mmol) Yb₂O₃ being used in place of Tm₂O₃. Plate-like colorless crystals were formed by slow evaporation of the reddish solution (pH = 5.5) at room temperature for one week. Yield: ca. 69% on the basis of the initial Yb₂O₃ input. C₇₂H₅₈N₁₆O₁₈Yb₂ (%): calcd. C 48.54, H 3.28, N 12.58; found C 48.67, H 3.38, N 12.84.

X-ray structural analyses

Suitable single crystals were selected under a polarizing microscope and fixed with epoxy cement on the tips of fine glass fibres, which were then mounted on a Bruker P4 diffractometer for cell determination and data collection. The lattice parameters were refined from the 2 ϑ values (10 - 25°) of 25 carefully centered reflections. The cell determination suggested that both title complexes are isostructural with the earlier-reported Er and Lu phen compounds of the general composition [Ln₂(phen)₄(H₂O)₄(OH)₂](phen)₂(NO₃)₄ with Ln =

Table 2a. Atomic parameters and equivalent isotropic displacement parameters (Å²) for non-hydrogen atoms in 1. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}	Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Tm	2i	0.55125(3)	0.61646(3)	0.60603(2)	0.0281(2)	C19	2i	0.9583(8)	0.6045(9)	0.7454(8)	0.042(2)
N1	2i	0.6330(7)	0.8278(7)	0.5467(6)	0.034(2)	C20	2i	1.043(1)	0.669(1)	0.6873(9)	0.053(3)
N2	2i	0.3873(7)	0.6873(7)	0.5061(5)	0.035(2)	C21	2i	1.0006(8)	0.699(1)	0.6042(8)	0.048(3)
N3	2i	0.6128(7)	0.4900(8)	0.7344(6)	0.038(2)	C22	2i	0.8682(8)	0.6807(9)	0.5863(7)	0.043(2)
N4	2i	0.7783(8)	0.6366(7)	0.6394(5)	0.035(2)	C23	2i	0.8281(8)	0.5872(8)	0.7168(6)	0.032(2)
N5	2i	0.7983(9)	0.7637(8)	0.9120(6)	0.046(2)	C24	2i	0.7378(9)	0.5090(8)	0.7675(6)	0.036(2)
N6	2i	0.9674(9)	0.9098(8)	0.8091(7)	0.052(2)	C25	2i	0.719(1)	0.693(1)	0.9603(9)	0.058(3)
N7	2i	0.433(1)	0.798(1)	0.8971(9)	0.071(3)	C26	2i	0.756(1)	0.662(1)	1.0524(9)	0.063(3)
N8	2i	0.1486(8)	0.3044(9)	0.6571(6)	0.050(2)	C27	2i	0.879(1)	0.708(1)	1.0938(8)	0.061(3)
C1	2i	0.7525(9)	0.9043(9)	0.5728(8)	0.043(2)	C28	2i	0.967(1)	0.784(1)	1.0441(8)	0.051(3)
C2	2i	0.806(1)	1.0020(9)	0.5220(9)	0.053(3)	C29	2i	1.099(1)	0.836(1)	1.0838(9)	0.065(3)
C3	2i	0.736(1)	1.021(1)	0.4407(9)	0.051(2)	C30	2i	1.183(1)	0.905(1)	1.0345(9)	0.063(3)
C4	2i	0.608(1)	0.9465(9)	0.4133(8)	0.044(2)	C31	2i	1.142(1)	0.932(1)	0.9397(8)	0.053(3)
C5	2i	0.523(1)	0.967(1)	0.3344(8)	0.054(3)	C32	2i	1.227(1)	1.004(1)	0.887(1)	0.061(3)
C6	2i	0.402(1)	0.898(1)	0.3145(8)	0.053(3)	C33	2i	1.183(1)	1.031(1)	0.799(1)	0.064(3)
C7	2i	0.347(1)	0.8026(9)	0.3734(7)	0.041(2)	C34	2i	1.052(1)	0.980(1)	0.7629(9)	0.056(3)
C8	2i	0.219(1)	0.736(1)	0.3604(7)	0.050(2)	C35	2i	1.012(1)	0.8855(9)	0.8978(7)	0.043(2)
C9	2i	0.1748(9)	0.6513(9)	0.4212(7)	0.039(2)	C36	2i	0.923(1)	0.8088(9)	0.9509(7)	0.043(2)
C10	2i	0.2625(8)	0.6279(8)	0.4927(7)	0.035(2)	O1	2i	0.3896(6)	0.5943(7)	0.6989(5)	0.042(1)
C11	2i	0.4290(8)	0.7763(8)	0.4484(6)	0.034(2)	O2	2i	0.6404(7)	0.7655(7)	0.7427(5)	0.046(2)
C12	2i	0.5610(9)	0.8499(8)	0.4687(7)	0.034(2)	O3	2i	0.4187(6)	0.4321(5)	0.5432(4)	0.033(1)
C13	2i	0.529(1)	0.411(1)	0.7776(8)	0.046(2)	O4	2i	0.373(2)	0.690(2)	0.877(1)	0.159(8)
C14	2i	0.564(1)	0.351(1)	0.8543(8)	0.057(3)	O5	2i	0.450(2)	0.843(1)	0.9795(9)	0.111(4)
C15	2i	0.688(1)	0.373(1)	0.8900(8)	0.054(3)	O6	2i	0.487(2)	0.857(1)	0.837(1)	0.131(6)
C16	2i	0.779(1)	0.453(1)	0.8455(7)	0.044(2)	O7	2i	0.1563(9)	0.4138(9)	0.6698(9)	0.077(3)
C17	2i	0.912(1)	0.478(1)	0.8756(8)	0.053(3)	O8	2i	0.0462(8)	0.2244(9)	0.6489(8)	0.076(3)
C18	2i	0.999(1)	0.551(1)	0.8284(8)	0.054(3)	O9	2i	0.2452(8)	0.2748(9)	0.6502(7)	0.065(2)

Er, Lu [8]. Therefore, the structure determinations were started by using the final coordinates of the non-hydrogen atoms in [Er₂(phen)₄(H₂O)₄(OH)₂](phen)₂(NO₃)₄ as initial positions. After several cycles of refinement, all hydrogen atoms of the 1,10-phenanthroline were given in their calculated positions ($d(\text{C-H}) = 0.93 \text{ \AA}$) except the hydroxo and aqua hydrogen atoms, which were located from the successive difference Fourier syntheses. The calculated hydrogen atoms were refined using a riding model, whereas the located H atoms were not refined since they unreasonably moved to or flew away from the covalently bonded atom. All the other atoms were finally refined with anisotropic displacement parameters by full-matrix least-squares technique using the SHELXL-97 program [10]. Detailed information about the crystal data and structure determinations are summarized in Table 1. The final positional and equivalent isotropic thermal parameters for non-hydrogen atoms are given in Table 2 and selected interatomic distances and bond angles in Table 3. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with Cam-

bridge Crystallographic Data Centre as supplementary publication nos. CCDC 180087 ([Tm₂(phen)₄(H₂O)₄(OH)₂](phen)₂(NO₃)₄), CCDC 180088 ([Yb₂(phen)₄(H₂O)₄(OH)₂](phen)₂(NO₃)₄). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

Results and Discussion

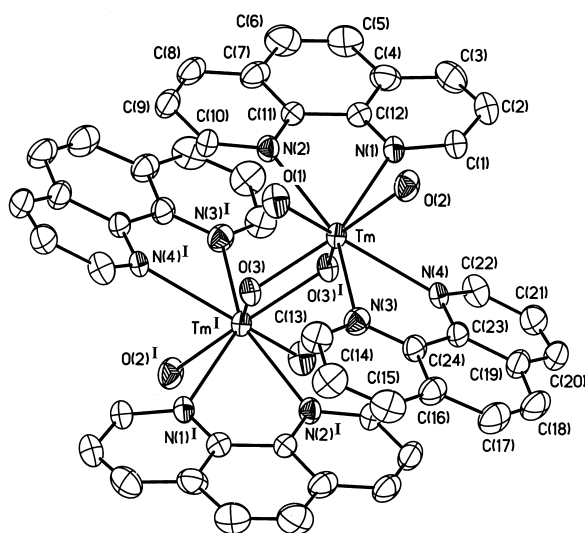
Structure description

Just as stated above, both title complexes are isostructural with the phen complexes [Ln₂(phen)₄(H₂O)₄(OH)₂](phen)₂(NO₃)₄ with Ln = Er, Lu [8] and are composed of the centrosymmetric dinuclear [Ln₂(phen)₄(H₂O)₄(OH)₂]⁴⁺ complex cations (Ln = Tm (1) and Yb (2)), NO₃⁻ anions and phen molecules.

The lanthanide atoms are each coordinated by two crystallographically distinct phen ligands, two H₂O molecules and two μ -OH groups to form

Table 2b. Atomic parameters and equivalent isotropic displacement parameters (Å²) for non-hydrogen atoms in 2. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}	Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Yb	2i	0.55100(2)	0.61585(2)	0.60597(2)	0.0271(1)	C19	2i	0.9597(7)	0.6054(7)	0.7441(6)	0.041(2)
N1	2i	0.6345(5)	0.8264(5)	0.5470(4)	0.035(1)	C20	2i	1.0439(8)	0.6679(8)	0.6874(7)	0.052(2)
N2	2i	0.3859(5)	0.6858(5)	0.5072(4)	0.032(1)	C21	2i	0.9965(8)	0.7076(8)	0.6073(8)	0.056(2)
N3	2i	0.6120(6)	0.4892(6)	0.7336(5)	0.038(1)	C22	2i	0.8694(7)	0.6905(7)	0.5830(5)	0.037(1)
N4	2i	0.7850(5)	0.6352(5)	0.6362(5)	0.036(1)	C23	2i	0.8280(7)	0.5865(7)	0.7163(6)	0.034(1)
N5	2i	0.7969(7)	0.7636(6)	0.9108(5)	0.047(1)	C24	2i	0.7366(7)	0.5090(6)	0.7672(5)	0.034(1)
N6	2i	0.9661(7)	0.9071(7)	0.8085(5)	0.048(2)	C25	2i	0.717(1)	0.691(1)	0.9607(7)	0.057(2)
N7	2i	0.435(1)	0.7994(9)	0.8960(8)	0.074(3)	C26	2i	0.754(1)	0.661(1)	1.0519(7)	0.064(2)
N8	2i	0.1494(6)	0.3034(6)	0.6567(5)	0.045(1)	C27	2i	0.879(1)	0.708(1)	1.0933(7)	0.063(2)
C1	2i	0.7523(7)	0.9039(7)	0.5736(6)	0.043(2)	C28	2i	0.9671(9)	0.7831(9)	1.0442(5)	0.049(2)
C2	2i	0.8057(8)	1.0017(7)	0.5219(7)	0.051(2)	C29	2i	1.099(1)	0.836(1)	1.0842(7)	0.070(3)
C3	2i	0.7346(9)	1.0196(7)	0.4412(7)	0.052(2)	C30	2i	1.182(1)	0.905(1)	1.0352(8)	0.070(3)
C4	2i	0.6067(9)	0.9447(7)	0.4155(6)	0.045(2)	C31	2i	1.1394(9)	0.9311(8)	0.9412(7)	0.051(2)
C5	2i	0.5223(9)	0.9654(8)	0.3345(6)	0.052(2)	C32	2i	1.227(1)	1.0060(9)	0.8874(8)	0.060(2)
C6	2i	0.398(1)	0.8956(9)	0.3157(7)	0.060(2)	C33	2i	1.182(1)	1.0317(9)	0.7985(8)	0.061(2)
C7	2i	0.3482(8)	0.8027(8)	0.3735(6)	0.043(2)	C34	2i	1.0517(9)	0.9815(8)	0.7631(7)	0.056(2)
C8	2i	0.2188(8)	0.7359(8)	0.3610(6)	0.047(2)	C35	2i	1.0096(8)	0.8847(7)	0.8980(5)	0.042(2)
C9	2i	0.1756(7)	0.6502(8)	0.4213(6)	0.043(2)	C36	2i	0.9213(9)	0.8085(8)	0.9513(6)	0.043(2)
C10	2i	0.2616(7)	0.6255(7)	0.4935(6)	0.038(1)	O1	2i	0.3896(5)	0.5924(6)	0.6983(4)	0.045(1)
C11	2i	0.4298(6)	0.7764(6)	0.4482(5)	0.032(1)	O2	2i	0.6393(5)	0.7642(5)	0.7426(4)	0.042(1)
C12	2i	0.5612(7)	0.8498(6)	0.4699(5)	0.033(1)	O3	2i	0.4185(4)	0.4314(4)	0.5425(3)	0.0315(9)
C13	2i	0.5300(9)	0.4124(8)	0.7759(6)	0.047(2)	O4	2i	0.377(2)	0.689(1)	0.8780(9)	0.175(8)
C14	2i	0.5632(9)	0.3505(9)	0.8545(6)	0.055(2)	O5	2i	0.449(1)	0.843(1)	0.9796(7)	0.116(4)
C15	2i	0.687(1)	0.3732(9)	0.8895(6)	0.053(2)	O6	2i	0.491(1)	0.859(1)	0.8348(8)	0.115(4)
C16	2i	0.7795(8)	0.4535(8)	0.8444(6)	0.041(2)	O7	2i	0.1564(7)	0.4134(7)	0.6693(7)	0.074(2)
C17	2i	0.9125(9)	0.4784(9)	0.8755(6)	0.052(2)	O8	2i	0.0462(6)	0.2243(7)	0.6486(7)	0.072(2)
C18	2i	0.9988(9)	0.5503(9)	0.8286(7)	0.056(2)	O9	2i	0.2454(6)	0.2754(7)	0.6508(5)	0.060(2)

Fig. 1. Ortep view of the dinuclear [Tm₂(phen)₄(H₂O)₄(OH)₂]⁴⁺ complex cations with displacement ellipsoids (45% probability) and atomic labelling.

Ln₂N₄O₄ tetragonal antiprisms, which are condensed via two common μ -OH groups into dinuclear [Ln₂(phen)₄(H₂O)₄(OH)₂]⁴⁺ complex cations centered at the crystallographic 1*h* sites (Fig. 1). The lanthanide atoms and the oxygen atoms of the coordinating water molecules and hydroxo groups are roughly in a common plane with the coordinating phen ligands arranged on both sides. Exhibiting strong deviation from coplanarity, the two crystallographically different phen ligands on the same side are warped in one direction. For the phen ligand containing N(1) and N(2), the dihedral angles between the central benzene and side pyridine fragments are 5.7(7)° and 5.0(6)° in 1 and 5.4(5)° and 5.0(6)° in 2. The distortion of the phen ligand containing N(3) and N(4) is more significant with the dihedral angles between the central benzene and the side pyridine fragments of 3.7(6)° and 9.5(5)° in 1 and 3.8(5)° and 6.9(5)° in 2. The Ln-O bond distances to the bridging hydroxo group are significantly shorter than those to the water molecules, and the latter in

Table 3. Selected interatomic distances (in Å) and bond angles (in degree) for 1 and 2.

– Compound 1 –				– Compound 2 –			
Tm-O1	2.342(6)	Tm-N4	2.460(8)	Yb-O1	2.331(5)	Yb-N4	2.538(6)
Tm-O2	2.350(7)	N7-O4	1.19(2)	Yb-O2	2.343(5)	N7-O4	1.22(2)
Tm-O3	2.204(6)	N7-O5	1.20(2)	Yb-O3	2.207(4)	N7-O5	1.21(1)
Tm-O3 ^I	2.226(6)	N7-O6	1.22(2)	Yb-O3 ^I	2.211(4)	N7-O6	1.25(1)
Tm-N1	2.549(7)	N8-O7	1.23(1)	Yb-N1	2.544(6)	N8-O7	1.24(1)
Tm-N2	2.523(7)	N8-O8	1.21(1)	Yb-N2	2.521(6)	N8-O8	1.22(1)
Tm-N3	2.537(8)	N8-O9	1.25(1)	Yb-N3	2.530(6)	N8-O9	1.23(1)
Tm...Tm ^I	3.647(1)			Yb...Yb ^I	3.636(1)		
O1/Tm/O2	74.4(2)	O3 ^I /Tm/N1	77.4(2)	O1/Yb/O2	74.5(2)	O3 ^I /Yb/N1	77.2(2)
O1/Tm/O3	78.8(2)	O3 ^I /Tm/N2	79.4(2)	O1/Yb/O3	78.8(2)	O3 ^I /Yb/N2	79.9(2)
O1/Tm/O3 ^I	141.4(2)	O3 ^I /Tm/N3	115.9(2)	O1/Yb/O3 ^I	141.4(2)	O3 ^I /Yb/N3	115.8(2)
O1/Tm/N1	115.1(2)	O3 ^I /Tm/N4	79.9(2)	O1/Yb/N1	115.7(2)	O3 ^I /Yb/N4	78.4(2)
O1/Tm/N2	75.2(2)	N1/Tm/N2	63.8(2)	O1/Yb/N2	74.7(2)	N1/Yb/N2	64.6(2)
O1/Tm/N3	78.5(3)	N1/Tm/N3	140.8(2)	O1/Yb/N3	78.5(2)	N1/Yb/N3	140.6(2)
O1/Tm/N4	135.5(2)	N1/Tm/N4	83.7(2)	O1/Yb/N4	136.9(2)	N1/Yb/N4	83.0(2)
O2/Tm/O3	148.5(2)	N2/Tm/N3	151.1(3)	O2/Yb/O3	148.6(2)	N2/Yb/N3	150.6(2)
O2/Tm/O3 ^I	141.6(2)	N2/Tm/N4	144.4(3)	O2/Yb/O3 ^I	141.5(2)	N2/Yb/N4	144.2(2)
O2/Tm/N1	71.9(2)	N3/Tm/N4	64.5(3)	O2/Yb/N1	71.9(2)	N3/Yb/N4	65.2(2)
O2/Tm/N2	106.2(3)	O4/N7/O5	119(1)	O2/Yb/N2	105.9(2)	O4/N7/O5	116(1)
O2/Tm/N3	77.6(3)	O4/N7/O6	121(1)	O2/Yb/N3	77.9(2)	O4/N7/O6	121(1)
O2/Tm/N4	74.3(2)	O5/N7/O6	120(1)	O2/Yb/N4	75.7(2)	O5/N7/O6	122(1)
O3/Tm/O3 ^I	69.2(2)	O7/N8/O8	120(1)	O3/Yb/O3 ^I	69.3(2)	O7/N8/O8	118.9(8)
O3/Tm/N1	136.1(2)	O7/N8/O9	120.5(9)	O3/Yb/N1	136.2(2)	O7/N8/O9	120.4(7)
O3/Tm/N2	82.3(2)	O8/N7/O9	120(1)	O3/Yb/N2	82.2(2)	O8/N7/O9	120.8(8)
O3/Tm/N3	81.1(2)	Tm/O3/Tm ^I	110.8(2)	O3/Yb/N3	80.9(2)	Yb/O3/Yb ^I	110.7(2)
O3/Tm/N4	116.4(2)			O3/Yb/N4	115.5(2)		

Symmetry code: (I) 1 - x, 1 - y, 1 - z.

turn are shorter than the Ln-N bonds (Table 3). The distance between two metal atoms in the complex cation is 3.647(1) Å and 3.636(1) Å for 1 and 2, respectively.

Along the [010] direction, the dinuclear complex cations are aligned so that the symmetry related phen neighbors containing N1 and N2 atoms are parallel and face opposite directions with the quinoline fragments partially engaged in π - π stacking interactions (the interplanar distance: 3.51 and 3.45 Å for 1 and 2, respectively).

Different from the coordinating phen ligands, the uncoordinating phen molecules show nearly perfect coplanarity. Through π - π interactions, two centrosymmetrically related phen molecules are stacked to form a (phen)₂ dimer with an interplanar separation of 3.56 Å.

As illustrated in Fig. 2, the (phen)₂ dimers and the complex cations are arranged in a sheet parallel to (10 $\bar{1}$) in such way that each (phen)₂ dimer is surrounded by four binuclear cations and each com-

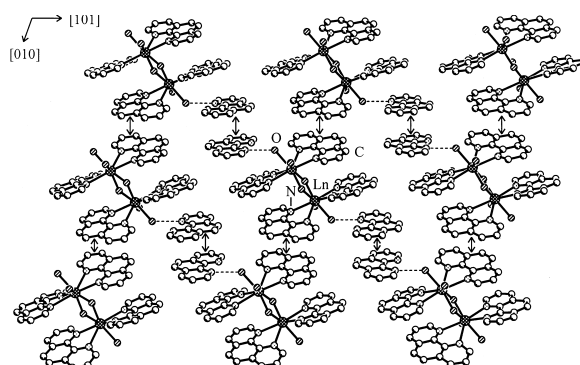


Fig. 2. The centrosymmetric dinuclear [Ln₂(phen)₄(H₂O)₄(OH)₂]⁴⁺ complex cations and (phen)₂ dimers are arranged in sheets parallel to (10 $\bar{1}$). π - π Stacking interactions and hydrogen bonds are indicated by double arrows and dashed lines, respectively. Hydrogen atoms are omitted for clarity.

plex cation is in turn encompassed by four (phen)₂ dimers and two symmetry related complex cations. The (phen)₂ dimers are associated with two cations

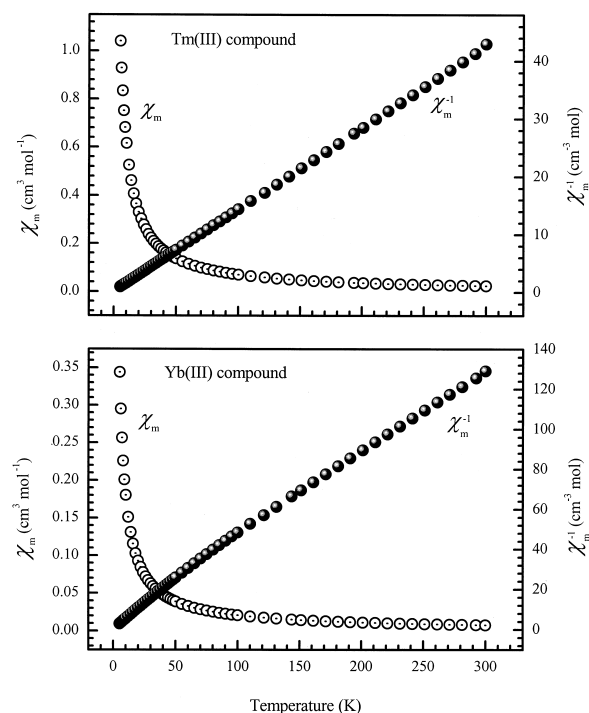


Fig. 3. Temperature dependences of the magnetic susceptibility χ_m ($\text{cm}^3 \text{mol}^{-1}$) (per Ln^{III} ion) and the inverse magnetic susceptibility χ_m^{-1} ($\text{cm}^3 \text{mol}$) (per Ln^{III} ion) for 1 (top) and 2 (bottom).

through hydrogen bonds between coordinating water O2 and pyridyl N5 atoms with $d(\text{O}2 \cdots \text{N}5) = 2.756$ and 2.738 \AA for 1 and 2, respectively. The next sheet is shifted along the [101] direction by $(\vec{a} + \vec{c})/2$. Additionally, the coordinating water molecules and hydroxo groups donate hydrogen atoms to both crystallographically different nitrate anions to form

hydrogen bonds ($d(\text{O} \cdots \text{O}) = 2.715 - 2.881 \text{ \AA}$, $\angle(\text{O}-\text{H} \cdots \text{O}) = 134 - 167^\circ$ for 1; $d(\text{O} \cdots \text{O}) = 2.678 - 2.881 \text{ \AA}$, $\angle(\text{O}-\text{H} \cdots \text{O}) = 145 - 161^\circ$ for 2). As a result, each complex cation is hydrogen bonded to four NO_3^- anions.

Magnetic properties

The temperature dependences of χ_m and χ_m^{-1} (inverse magnetic susceptibility per Ln³⁺ ion) are shown in Fig. 3. The Tm complex is paramagnetic and the magnetic susceptibility increases with decreasing temperature, obeying the Curie-Weiss law with the Curie constant of $7.10 \text{ cm}^3 \text{mol}^{-1} \text{K}$ and the Weiss constant $\Theta = -1.7 \text{ K}$. At room temperature, the effective magnetic moment is 7.51 B.M. close to 7.6 B.M. expected for the free Tm³⁺ ion [9]. Over the temperature range 70 - 300 K, the paramagnetic behavior of the Yb compound follows the Curie-Weiss law with the Curie constant of $2.47 \text{ cm}^3 \text{mol}^{-1} \text{K}$ and the Weiss constant $\Theta = -19.2 \text{ K}$. The effective magnetic moment at room temperature is 4.32 B.M. close to 4.5 B.M. expected for the free Yb³⁺ ion model based on the $^2F_{7/2}$ free ion ground term [9]. However, the χ_m^{-1} vs. T plot of the Yb compound exhibits a slight downward curvature from linearity below 70 K, suggesting weak ferrimagnetic behavior.

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