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 \(\text{Ln} = \text{Tm}, \text{Yb}\)

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Lanthanide, Dinuclear Complexes, \(\pi-\pi\) 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 \(\text{Ln} = \text{Tm} (1), \text{Yb} (2)\) were prepared by reactions of the corresponding lanthanide nitrate and phenanthroline monohydrate in \(\text{CH}_3\text{OH/H}_2\text{O}\) at \(p\text{H} = 5.5\). They crystallize in the triclinic space group \(\text{P}\bar{1}\) (no. 2) with the cell dimensions: \(a = 11.233(1), b = 11.456(1), c = 14.011(2) \text{ Å}, \alpha = 93.91(1)^\circ, \beta = 98.20(1)^\circ, \gamma = 108.21(1)^\circ, V = 1683.0(3) \text{ Å}^3; Z = 1\) for 1 and \(a = 11.236(1), b = 11.480(2), c = 13.986(2) \text{ Å}, \alpha = 93.91(1)^\circ, \beta = 98.17(1)^\circ, \gamma = 108.33(1)^\circ, V = 1682.9(3) \text{ Å}^3; Z = 1\) for 2. The crystal structures are composed of the hydroxo bridged dinuclear \([\text{Ln}_2(\text{phen})_4(\text{H}_2\text{O})_4(\text{OH})_2]^{4+}\) complex cations, hydrogen bonded \(\text{NO}_3^-\) anions and \(\pi-\pi\) stacking (phen)\(_2\) dimers. The lanthanide atoms are each surrounded by two phen ligands, two \(\text{H}_2\text{O}\) molecules and two \(\mu-\text{OH}\) groups to complete a tetragonal antiprismatic \(\text{LnN}_4\text{O}_4\) coordination. Via two common \(\mu-\text{OH}\) groups, two neighboring tetragonal antiprisms are condensed to form a centrosymmetric dinuclear \([\text{Ln}_2(\text{phen})_4(\text{H}_2\text{O})_4(\text{OH})_2]^{4+}\) complex cation. The complex cations and (phen)\(_2\) dimers are assembled via \(\pi-\pi\) stacking interactions and hydrogen bondings into 2D layers parallel to \((10\bar{1})\), between which the hydrogen bonded \(\text{NO}_3^-\) 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.