



Heteronuclear M(II)–Ln(III) (M = Co, Mn; Ln = La, Pr, Sm, Gd, Dy and Er) coordination polymers: Synthesis, structures and magnetic properties

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ABSTRACT

Thirteen novel 3d–4f heteronuclear coordination polymers based on the pyridine-2,6-dicarboxylic acid (H₂pda) and imidazole ligands, Hlm[(pda)₃MLn(Im)₂(H₂O)₂·3H₂O (Im = imidazole; M = Co, Ln = Pr (**1**), Gd (**2**), Dy (**3**), Er (**4**); M = Mn, Ln = Pr (**5**), Sm (**6**), Gd (**7**), Dy (**8**), Er (**9**)), Hlm[(pda)₃CoSm(Im)₂(H₂O)₂·2H₂O (**10**), [(Im)₄M(H₂O)₂][(pda)₄La₂(H₂O)₂·2H₂O (M = Co (**11**), Mn (**12**)), and [(pda)₆Co₃Pr₂(H₂O)₆·6H₂O (**13**), have been prepared and structurally characterized. X-ray crystallographic analyses revealed that these complexes display four different types of structures. Complexes **1–9** are isostructural, and possess 1-D chain structures constructed by alternately arrayed nine-coordinated Ln(III) (Ln = Pr, Sm, Gd, Dy, Er) and six-coordinated M(II) (M = Mn, Co) ions. Complex **10** exhibits a unique one-dimensional structure, in which two independent chains are parallel viewed down the *a*-axis and anti-parallel viewed down the *c*-axis. Complexes **11** and **12** are isostructural and display 1-D homometallic chain structures. Complex **13** is a 3D framework fabricated through PrN₃O₆ and CoO₆ polyhedrons as building blocks. The variable-temperature solid-state dc magnetic susceptibilities of complexes **2**, **3**, **4**, **9** and **13** have been investigated. Antiferromagnetic exchange interactions were determined for these five complexes.

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1. Introduction

The design and synthesis of 3d–4f heterometallic coordination polymers have attracted increasing attention [1–5]. The interests in these polymers span from pure academic aspects of chemistry and physics to applications as functional materials in magnetism [6–14], molecular adsorption [15–17], catalysis [18,19], and light conversion devices [20–22]. However, the preparation of 3d–4f coordination polymers has certain difficulties. There are two important factors that cause the synthetic challenge. Firstly, the variable and high coordination numbers of the trivalent lanthanide ions make the coordination geometries of the polymers uncontrollable. Secondly, since rare earth metal ions behave as hard acid and prefer oxygen to nitrogen atoms, while 3d transition metal ions have a strong tendency to coordinate N-donors as well as O-donors, it is quite possible that the competition between 3d and 4f metals in coordinating to the same ligand gives rise to homometallic coordination polymers rather than heterometallic ones. Therefore, one of the synthetic strategies in building such polymers is to employ appropriate bridging ligands, which have

bonding site with differential affinities in order to discriminate different metal ions. To date, a few types of multidentate ligands containing N- and O-donors, e.g., pyridine-dicarboxylic acids [23–26,7,15], amino acid [27,13], Schiff-base [1,6], etc., have been reported in the literature. Among them, pyridine-2,6-dicarboxylic acid (H₂pda) is a good ligand for the preparation of high dimensional 3d–4f metal coordination polymers, because H₂pda displays several coordination modes, such as O-unidentate [28], O, N-bidentate [29,30], O, N, O-tridentate [28,31–35], (O, N) O-bidentate bridging [36,37], (O, N, O) O and O, N, μ -O-tridentate bridging [38–40]. The diverse coordination modes of H₂pda largely contributed to the formation of the aesthetically pleasing structures. Moreover, when coordinating to 4f metal ions, pda²⁻ adopts a tridentate mode: the N atom coordinates with two O atoms from two adjacent carboxylic groups (each carboxylic group provides one O atom), while the other O atoms of the carboxylic groups coordinate to 3d metal ions. The use of H₂pda had previously given a number of heteronuclear coordination polymers [7,15,23–26]. Remarkably, it is found that the polymers with designed structural motifs have been resulted by dexterously combining H₂pda with another properly selected ancillary ligand [41].

We are interested in the combination of H₂pda with imidazole. H₂pda could simultaneous chelate with lanthanide ions and bridge transition metal ions, and imidazole tends to coordinate with transition metal ions, preventing the formation of homometallic

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coordination polymers. Employment of imidazole as an ancillary ligand could also prevent H₂O from coordinating with metal ions and increase the thermal stability of the resulting polymers [42].

Complexes containing the H₂pda and imidazole ligands have not been reported before. Heterometallic 3d–4f complexes containing both lanthanide (4f) and transition (3d) metals are mostly focused on the lanthanide–copper (Ln–Cu) system [1,43], while those with lanthanide–cobalt [44,15,24] (or manganese [13]) metals are scarce. In the present work, we have used H₂pda in combination with imidazole for the synthesis of some interesting 1-D and 3-D Co(II)–Ln(III) and Mn(II)–Ln(III) coordination polymers.

The results of present investigation provide 13 interesting 3d–4f coordination polymeric complexes: Hlm[(pda)₃MnLn(Im)₂(H₂O)₂]₂·3H₂O (H₂pda = pyridine-2,6-dicarboxylic acid, Im = imidazole, M = Co, Ln = Pr (**1**), Gd (**2**), Dy (**3**), Er (**4**); M = Mn, Ln = Pr (**5**), Sm (**6**), Gd (**7**), Dy (**8**), Er (**9**)), Hlm[(pda)₃CoSm(Im)₂(H₂O)₂]₂·2H₂O (**10**), [(Im)₄M(H₂O)₂][(pda)₄La₂(H₂O)₂]₂·2H₂O (M = Co (**11**), Mn (**12**)), and [(pda)₆Co₃Pr₂(H₂O)₆]₆·6H₂O (**13**). The magnetic properties of **2**, **3**, **4**, **9** and **13** have been investigated.

2. Experimental

2.1. General procedure

Ln(NO₃)₃·6H₂O was prepared by dissolving Ln₂O₃ in dilute nitric acid followed by drying and crystallization. Other chemicals were purchased from commercial suppliers and used without further purification. The C, H and N microanalyses were carried out with a Carlo-Erba EA1110 CHNO-S elemental analyzer. FT-IR spectra were recorded from KBr pellets in the range of 400–4000 cm⁻¹ on a Nicolet MagNa-IR500 spectrometer. Crystal determination was performed with a Bruker SMART APEX II CCD diffractometer equipped with graphite-monochromatized Mo K α radiation (λ = 0.71073 Å). Variable-temperature magnetic susceptibilities were measured with a Quantum Design MPMS-7 SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants for all constituent atoms. The elemental analysis results are listed in Table 1.

2.2. Crystal structure refinement

Data were collected at room temperature; the ω – 2 θ scan technique was applied. The structures were solved by direct methods using SHELXS-97 [45] and refined on F² using full-matrix least-squares with SHELXL-97 [46,47]. Crystallographic data together with refinement details for the complexes reported in this work were

Table 1
Elemental analytic data of the complexes.

Complex	% C		% H		% N	
	Found	Calc.	Found	Calc.	Found	Calc.
1 C ₃₀ H ₃₂ CoPrN ₉ O ₁₇	36.27	36.38	3.25	3.26	12.19	12.73
2 C ₃₀ H ₃₂ CoGdN ₉ O ₁₇	35.46	35.79	3.14	3.20	11.97	12.52
3 C ₃₀ H ₃₂ CoDyN ₉ O ₁₇	34.98	35.60	3.19	3.19	11.81	12.46
4 C ₃₀ H ₃₂ CoErN ₉ O ₁₇	35.15	35.44	3.20	3.17	12.04	12.40
5 C ₃₀ H ₃₂ MnPrN ₉ O ₁₇	36.05	36.53	3.34	3.27	12.09	12.78
6 C ₃₀ H ₃₂ MnSmN ₉ O ₁₇	35.61	36.18	3.02	3.24	11.92	12.66
7 C ₃₀ H ₃₂ MnGdN ₉ O ₁₇	35.51	35.93	2.91	3.22	11.85	12.57
8 C ₃₀ H ₃₂ MnDyN ₉ O ₁₇	35.84	35.74	3.07	3.20	11.83	12.51
9 C ₃₀ H ₃₂ MnErN ₉ O ₁₇	35.30	35.58	3.17	3.18	11.81	12.45
10 C ₃₀ H ₃₀ CoSmN ₉ O ₁₆	36.11	36.70	3.22	3.08	12.57	12.84
11 C ₄₀ H ₄₀ La ₂ CoN ₁₂ O ₂₂	34.47	34.88	2.96	2.93	11.89	12.20
12 C ₄₀ H ₄₀ La ₂ MnN ₁₂ O ₂₂	35.33	34.98	2.71	2.94	12.01	12.24
13 C ₄₂ H ₄₂ Co ₃ N ₆ O ₃₆ P ₇	29.07	30.29	2.78	2.54	4.99	5.05

summarized in Table 2. Selected bond lengths and angles for complexes **1–13** were given in Supplementary data.

2.3. Preparations

2.3.1. Synthesis of Hlm[(pda)₃CoLn(Im)₂(H₂O)₂]₂·3H₂O (Ln = Pr (**1**), Gd (**2**), Dy (**3**), Er (**4**))

A mixture solution of H₂pda (0.0334 g, 0.2 mmol), Co(NO₃)₂·6H₂O (0.0291 g, 0.1 mmol), Ln(NO₃)₃·6H₂O (0.0217–0.238 g, 0.05 mmol), Im (0.0382 g, 0.56 mmol), H₂O/C₂H₅OH (3 mL, v/v = 2:1) was sealed in a Pyrex-tube (8 mL). The tube was heated at 90 °C for 4 days under autogenously pressure. The resultant solution was gradually cooled to room temperature at a rate of 5 °C/h. Pink crystals were obtained. The crystals were collected by filtration, washed with H₂O (3 mL) and dried in air. IR (KBr, cm⁻¹): (**1**): 3454 (br), 1616 (s), 1572 (s), 1433 (s), 1389 (s), 1273 (s), 1186 (s), 1072 (s), 1014 (s), 769 (s), 727 (s), 659 (s); (**2**): 3417 (br), 1636 (s), 1581 (s), 1431 (s), 1384 (s), 1277 (s), 1069 (s), 1021 (s), 731 (s), 662 (s); (**3**): 3372 (br), 1636 (s), 1582 (s), 1435 (s), 1389 (s), 1281 (s), 1188 (s), 1072 (s), 1022 (s), 922 (s), 733 (s), 664 (s); (**4**): 3428 (br), 1656 (s), 1569 (s), 1384 (s), 1269 (s), 1204 (s), 1078 (s), 1020 (s), 935 (s), 770 (s), 734 (s), 661 (s).

2.3.2. Synthesis of Hlm[(pda)₃MnLn(Im)₂(H₂O)₂]₂·3H₂O (Ln = Pr (**5**), Sm (**6**), Gd (**7**), Dy (**8**), Er (**9**))

Complexes **5–9** were prepared in the same way as for **1**, using Mn(CH₃COO)₂·4H₂O (0.0252 g, 0.1 mmol) instead of Co(NO₃)₂·6H₂O as the 3d metal source. Light-color crystals were obtained. IR (KBr, cm⁻¹): (**5**): 3442 (br), 2692 (s), 1431 (s), 1388 (s), 1276 (s), 1189 (s), 1032 (s), 1018 (s), 916 (s), 768 (s), 728 (s), 661 (s); (**6**): 3318 (br), 1616 (s), 1572 (s), 1433 (s), 1377 (s), 1279 (s), 1192 (s), 1074 (s), 1018 (s), 918 (s), 733 (s), 662 (s); (**7**): 3422 (br), 1628 (s), 1572 (s), 1433 (s), 1389 (s), 1275 (s), 1190 (s), 1070 (s), 1018 (s), 920 (s), 733 (s), 660 (s); (**8**): 3435 (br), 1628 (s), 1572 (s), 1435 (s), 1375 (s), 1277 (s), 1192 (s), 1070 (s), 1018 (m), 920 (s), 772 (s), 735 (s), 662 (s); (**9**): 3513 (br), 1643 (s), 1570 (s), 1434 (s), 1434 (s), 1400 (s), 1280 (s), 1195 (s), 1100 (s), 1078 (s), 1022 (s), 924 (s), 734 (s), 660 (s).

2.3.3. Synthesis of Hlm[(pda)₃CoSm(Im)₂(H₂O)₂]₂·2H₂O (**10**)

Complex **10** was prepared in the same way as for **1**, using Sm(NO₃)₃·6H₂O (0.0237 g, 0.05 mmol) as the Ln source. Pink crystals were obtained. IR (KBr, cm⁻¹): 3364 (br), 1616 (s), 1574 (s), 1435 (s), 1393 (s), 1277 (s), 1188 (s), 1072 (s), 1018 (s), 918 (s), 768 (s), 729 (s), 660 (s).

2.3.4. Synthesis of [(Im)₄Co(H₂O)₂][(pda)₂La(H₂O)₂]₂·2H₂O (**11**)

Complex **11** was prepared in the same way as for **1**, using La(NO₃)₃·6H₂O (0.0215 g, 0.05 mmol) as the Ln source. Selected IR data (KBr, cm⁻¹): 3386 (br), 1623 (s), 1607 (s), 1580 (s), 1435 (s), 1393 (s), 1369 (s), 1275 (s), 1192 (s), 1074 (s), 1016 (s), 917 (s), 763 (s), 730 (s), 658 (s).

2.3.5. Synthesis of [(Im)₄Mn(H₂O)₂][(pda)₂La(H₂O)₂]₂·2H₂O (**12**)

Complex **12** was prepared in the same way as for **11**, using Mn(CH₃COO)₂·4H₂O (0.0258 g, 0.05 mmol) instead of Co(NO₃)₂·6H₂O as the 3d metal source. Selected IR data (KBr, cm⁻¹): 3380 (br), 1623 (s), 1436 (s), 1392 (s), 1369 (s), 1275 (s), 1192 (s), 1073 (s), 1016 (s), 918 (s), 763 (s), 742 (s), 659 (s).

2.3.6. Synthesis of [(pda)₆Co₃Pr₂(H₂O)₆]₆·6H₂O (**13**)

Complex **13** was prepared in the same way as for **1**, by reducing the amount of imidazole from 0.56 mmol to 0.4 mmol. IR (KBr, cm⁻¹): 3417 (br), 1616 (s), 1446 (s), 1379 (s), 1281 (s), 1198 (s), 1084 (s), 1022 (s), 863 (s), 775 (s), 721 (s), 667 (s).

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