Inorganic Chemistry Article

Inorg. Chem. **2009**, *48*, 11543–11550 **11543**
DOI: 10.1021/ic901066v

Cerium(IV)−Lanthanide(III)−Pyridine-2,6-dicarboxylic Acid System: Coordination Salts, Chains, and Rings

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Received June 3, 2009

A series of new heterometallic compounds containing cerium(IV) and lanthanide(III) with pyridine-2,6-dicarboxylic acid (dipicH_2) have been synthesized. Depending on the Ln^{III} ion and preparation conditions, we obtained four types of compounds. Type-I: one-dimensional coordination polymer, $[Ln(dipicH)(H_2O)_4Ce(dipic)_3]\cdot 7H_2O$; Ln = La (**1**), Ce (**2**), or Pr (**3**). Type-II: ionic compound, $[Ln(dipicH)(H_2O)_6][Ce(dipic)_3]\cdot 7H_2O$; Ln = Nd (**4**), Sm (**5**), Eu (**6**), Gd (**7**), or Dy (**8**). Type-III: octanuclear cluster incorporating a six-membered coordination ring, $[Ln(H_2O)_7Ln(dipic)(H_2O)_4(Ce(dipic)_3)_2]_2\cdot nH_2O$; Ln = La (**9**) *n* = 24, Ce (**10**) *n* = 24, Pr (**11**) *n* = 24, or Nd (**12**) *n* = 26. Type-IV: hexanuclear cluster incorporating a four-membered coordination ring, $[(Ln(H_2O)_5)_2(Ce(dipic)_3)_4(2H^+)]\cdot nH_2O$; Ln = Nd (**13**) *n* = 34, Sm (**14**) *n* = 26, Eu (**15**) *n* = 26, or Gd (**16**) *n* = 26. Crystal structures were determined for compounds **1**−**16**. Tb and heavier lanthanides all form compounds isomorphous with Type-IV compounds. The observed structural variety is a consequence of the interplay of lanthanide contraction and kinetic effects involving water molecules, free as well as clusters, ranging in size from 6 to 26. A metal-centered luminescence sensitized by dipic ligand was observed in compounds containing Eu^{III} and Dy^{III} ions. Direct chelation, as opposed to bridging coordination, leads to enhanced luminescence. Resolved EPR spectra were observed for the Gd^{III} compounds which are dependent on the coordination environment.

Introduction

Studies on coordination polymers as well as clusters containing lanthanides (Ln) are of current interest because of their diverse structural, spectral, and magnetic properties.[1] The properties of these compounds can be altered by incorporating extra metal ions in the clusters or coordination networks.[2] We have been working with heterometallic coordination compounds of cerium(IV) and alkaline earth−transition metals with dipicH_2 (dipicH_2 = dipicolinic acid).[3] Most of those compounds form coordination polymers with Ce^{IV} in all of them existing as $[Ce(dipic)_3]^{2-}$. This prompted us to study the chemistry of cerium(IV)-dipic in combination with Ln^{III} ions instead of alkaline earth or transition metals.

The reports of metal organic compounds containing multiple lanthanide ions are not common in the literature.[4] Compounds that contain cerium atoms are comparatively less common. In one compound, Ce^{III} and Gd^{III} were

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coordinated to porphyrin and phthalocyanine ligands to form a metal−metal triple-decker sandwich system.[4n] Another compound contains cerocene and $Yb(THF)_6$ units.[4j] Reports of mixed valent cerium coordination compounds are also rare.[3b,5] Further, there are only a few reports covering the entire lanthanide series for a given ligand.[6] These studies showed that the Ln^{III} ions may be classified into three groups according to their ionic size and that they usually form different coordination networks with a ligand that is sufficiently flexible. The present study on bimetallic coordination compounds presents a somewhat different situation. The presence of $Ce(dipic)_3^{2-}$ as a common factor in these compounds, because of the strong affinity between Ce^{4+} and $dipic^{2-}$, allows the difference in preference for water and dipic along the Ln^{III} series to manifest itself leading to the preparation of one-dimensional coordination polymers as well as a variety of zero-dimensional compounds.

Recent times have seen a surge in the structural characterization of water clusters in organic as well as metal organic compounds.[7] Small water clusters, $(H_2O)_n$ (n = 1−10) are very common in hydrates, and these clusters are stabilized by the H-bonds formed with donors or acceptors present on the molecules present in the host crystal. Higher-order water clusters are comparatively less numerous and are less stable due to the large size and relatively less number of H-bonds between water molecules and hosts. All compounds described in this paper contain a large number of lattice water molecules that aggregate together to form water cluster of diverse dimensions, viz., $(H_2O)_6$, $(H_2O)_{14}$, and $(H_2O)_{26}$.

Experimental Section

Synthesis. All chemicals were reagent grade commercial samples and were used without further purification.

$[Ln(dipicH)(H_2O)_4Ce(dipic)_3]\cdot 7H_2O$; Ln = La (**1**), Ce (**2**), or Pr (**3**). A similar procedure was employed for all compounds using hydrated nitrate salts as a source for Ln^{III}. In a typical experiment, solid $dipicH_2$ (0.672 g, 4.02 mmol) was added to a solution of $(NH_4)_2Ce(NO_3)_6$ (0.548 g, 1.00 mmol) and $La(NO_3)_3\cdot 6H_2O$(0.433 g, 1.00 mmol) in 15 mL of water. The $dipicH_2$ dissolves on stirring, and the resulting solution was stirred for 10 min to get a yellow precipitate, which was filtered and dried. The precipitate was recrystallized from hot water to get crystals of **1** suitable for X-ray data collection.

$[Ln(dipicH)(H_2O)_6][Ce(dipic)_3]\cdot 7H_2O$; Ln = Nd (**4**), Sm (**5**), Eu (**6**), Gd (**7**), or Dy (**8**). The same procedure as described above for **1** was used. The only difference was the use of 0.51 mmol Eu_2O_3 in 2 mL of 1N HNO_3 for **6** and 0.50 mmol Dy_2O_3 in 6 mL of 1N HNO_3 for **8**.

$[Ln(H_2O)_7Ln(dipic)(H_2O)_4(Ce(dipic)_3)_2]_2\cdot nH_2O$; Ln = La (**9**) n = 24, Ce (**10**) n = 24, Pr (**11**) n = 24, or Nd (**12**) n = 26. For compounds **9**, **11**, and **12**, the procedure was essentially the same as that described above for **1** except for the use of 3.00 mmol of $dipicH_2$. Compound **10** was prepared by a different procedure: To a 10 mL aqueous solution of $(NH_4)_2Ce(NO_3)_6$ (0.550 g, 1.00 mmol) and $CoCl_2\cdot 6H_2O$ (0.238 g, 1.00 mmol), 20 mL methanolic solution of $dipicH_2$ (0.500 g, 2.99 mmol) was added and stirred for about 1 h. An orange-yellow precipitate that formed was separated, redissolved in hot water,and filtered when hot, and the filtrate was allowed to evaporate at room temperature to obtain pale red crystals of **10**.

$[(Ln(H_2O)_5)_2(Ce(dipic)_3)_4(2H^+)]\cdot nH_2O$; Ln = Nd (**13**) n = 34, Sm (**14**) n = 26, Eu (**15**) n = 26, or Gd (**16**) n = 26. The same procedure as described above for **1** was followed except for the following changes: 3.00 mmol of dipicH2 for all, 0.50 mmol of $Nd(NO_3)_3\cdot 6H_2O$ for **13** and 0.51 mmol of Eu_2O_3 in 1N HNO_3 for **15**.

The color, yield, IR, and CHN data are presented in Table S1 of the Supporting Information.

Physical Measurements. IR spectra were recorded on a Jasco 5300 FT/IR infrared spectrometer. C, H, and N analysis was performed on a PerkinElmer 240C elemental analyzer. EPR spectra were measured on a JEOL JES−FA 200 spectrometer. Electronic reflectance spectra were measured by using a Shimadzu UV-3100 spectrometer equipped with an ISR-3100 integrating sphere attachment. Luminescence spectra were measured for polycrystalline samples using a Jobin Yvon Horiba FluoroMax-3 spectrofluorometer. Thermogravimetric analysis was performed by using a NETZSCH STA 409 PC/PG instrument. X-ray powder diffractograms were measured (Cu Kα) using a PW3710 model Philips Analytical X-ray diffractometer.

X-ray Crystallography. X-ray data were collected on a Bruker SMART APEX CCD X-ray diffractometer, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Data were reduced using SAINTPLUS[8], and a multiscan absorption correction using SADABS[9] was performed. The structure was solved using SHELXS-97[10], and full matrix least-squares refinement against F^2 was carried out using SHELXL-97.[10] All ring hydrogen atoms were assigned on the basis of geometrical considerations and were allowed to ride upon the respective carbon atoms. All hydrogen atoms were assigned fixed U_{iso} values, equal to 1.2 U_{eq} of the parent atom for ring atoms and 1.5 for carboxylic and water hydrogen atoms. Crystallographic data for a representative set of four compounds are listed in Table 1. Data for all compounds, ORTEP drawings, and packing diagrams are included in Table S2−S4 and Figures S1−S18 of the Supporting Information. Bond lengths in the Ln^{III} polyhedra in all 16 compounds are compared in Table S5 of the Supporting Information.

Results and Discussion

Synthesis. All compounds were prepared by the self-assembly method by mixing the reagents in aqueous media. The initial precipitates formed in all reactions were redissolved in hot water and allowed to evaporate at room temperature in an open container to get the crystals of the respective compounds. While the procedure employed is simple and similar for all compounds, the product obtained is controlled by the relative amounts of the reactants. For the preparation of compounds **1**−**8**, the preparative solution contained Ln^{III}, Ce^{IV}, and $dipicH_2$

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Table 1. Crystallographic Data for Representative Compounds

	1	**4**	**9**	**13**
chemical formula	$C_{28}H_{35}CeLaN_4O_{27}$	$C_{28}H_{39}CeN_4NdO_{29}$	$C_{98}H_{134}Ce_4La_4N_{14}O_{102}$	$C_{84}H_{126}Ce_4N_{12}Nd_2O_{92}$
formula weight	1138.62	1179.99	4256.31	3624.91
space group (no.)	$P\bar{1}$ (2)	$P\bar{1}$ (2)	$P\bar{1}$ (2)	$P\bar{1}$ (2)
a (Å)	12.8174(13)	12.101(3)	14.8714(9)	14.3621(12)
b (Å)	13.1120(13)	12.923(4)	15.1654(9)	16.2103(13)
c (Å)	13.1547(18)	14.729(4)	17.5244(11)	17.1486(14)
α (deg)	97.825(2)	109.869(4)	106.6350(10)	115.6520(10)
β (deg)	119.1350(10)	105.466(4)	100.6060(10)	113.9320(10)
γ (deg)	90.810(2)	99.961(4)	100.7950(10)	91.8990(10)
V (Å)	1904.8(4)	1997.6(9)	3599.3(4)	3182.2(5)
Z	2	2	1	1
T (°C)	25(2)	25(2)	−173(2)	−173(2)
D_{calcd} (g cm^{-3})	1.983	1.962	1.964	1.891
μ (cm^{-1})	2.394	2.520	2.523	2.328
$R(F_o^2)$ [$I > 2\sigma(I)$]^a	0.0348	0.0320	0.0385	0.0596
$R_w(F_o^2)$ (all data)^b	0.0944	0.0844	0.0909	0.1522

$^a R = \sum \| F_o| - |F_c\| / \sum |F_o|$. $^b R_w = [\sum w(F_o^2 - F_c^2)^2 / \sum (wF_o^4)]^{1/2}$.

in the molar ratio of 1:1:4. The same ratio is maintained in the crystals of all eight compounds. La^{3+}, Ce^{3+}, and Pr^{3+} (compounds **1**, **2**, and **3**, respectively) form isomorphous 1D coordination polymers, while Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Dy^{3+} (compounds **4**, **5**, **6**, **7**, and **8**, respectively) form ionic compounds instead of coordination polymers. Crystals of compounds **9**−**12** contain Ln^{III} (La/Ce/Pr/Nd), Ce^{IV}, and dipicH_2 in the molar ratio of 1:1:3.5, forming six-membered ring structures. The preparative solutions for compounds **9**, **11**, and **12** contained the above reagents in the molar ratio of 1:1:3. However, the Ce^{III} in compound **10** was generated by reduction of Ce^{IV} by Co^{II}. The Co(II) salt was used in this preparation initially with a view to prepare a Co^{II}/Ce^{IV} heterometallic compound because the Ce^{IV}/Co^{II} potential was not considered favorable for the reduction of Ce^{IV}. However, the reduction under the conditions of the experiment was confirmed by measuring the magnetic susceptibility of the preparative solutions. The redox process will greatly affect the solution susceptibility because Co^{III} will be diamagnetic and Co^{II} will have a magnetic moment corresponding to three unpaired electrons, and Ce^{III}, having one unpaired electron, has a low moment due to spin−orbit effects. It was found that in aqueous solution, the addition of ammonium ceric nitrate to cobalt(II) chloride solutions brings about expected change in magnetic susceptibility[11] in the presence as well as the absence of dipicH_2, while in neat methanol, the change is observed only in the presence of dipicH_2. The preparative solutions contained methanol and water. It is also possible that part of the Ce^{III} comes from the slow oxidation of water[12] by Ce^{IV}. The introduction of Ce^{III} directly through the use of cerium(III) nitrate had resulted in an entirely different compound containing a giant water cluster.[3b] Crystals of compounds **13**−**16** contain Ln^{III} (Nd/Sm/Eu/Gd), Ce^{IV}, and dipicH_2 in the molar ratio of 1:2:6, forming four-membered ring structures. In the case of compound **13**, the preparative solutions also contained the reagents in the same ratio, while 14, **15**, and **16** were obtained only when the Ln^{III} component was doubled. Only in the case of Nd did the use of different ratios (1:1:3 or 1:2:6) yield different products (compounds **12** and **13**). The initial precipitate formed during the reaction was confirmed to have the same structure as that of crystal by powder X-ray diffraction, except in the preparation of compound **4**, where it was found that the structure of the precipitate was polymeric as that of compounds **1**−**3**. In the case of **9**, **11**, **12**, and **13**, because of very low crystallanity of the precipitate and instability of crystals, the comparisons were not made.

Structures of [Ln(dipicH)(H_2O)$_4$Ce(dipic)$_3$]·7H_2O; Ln = La (1), Ce (2), or Pr (3). Compounds **1**−**3** are isomorphous one-dimensional coordination polymers made up of alternating $[Ln(dipicH)(H_2O)_4]^{2+}$ and $[Ce(dipic)_3]^{2-}$ units. Two out of the six free carbonyl oxygen atoms of the tris-chelate, $[Ce(dipic)_3]^{2-}$, are coordinated to adjacent $[Ln(dipicH)(H_2O)_4]^{2+}$ units leading to the formation of a one-dimensional chain (Figure 1). Both metal centers are nine-coordinate, having distorted tricapped trigonal prismatic coordination geometry. Selected geometrical parameters are given in Tables S6−S8 of the Supporting Information. In these structures, because Ln is in a +3 oxidation state, charge balance requires protonation of dipic to form $[Ln(dipicH)(H_2O)_4]^{2+}$ or protonation of a lattice water molecule. The former arrangement is probably the more stable one. However, we were unable to locate the correct position of the acidic hydrogen atom. One of the coordinated water molecules was disordered over two positions in all structures.

In all compounds there exist seven solvent water molecules in the asymmetric unit. Out of the seven, three are H-bonded to each other, and their symmetry related partners to form a planar water hexamer (Figure 2a). The hexamer has a near-square core made up of two symmetry related water molecules and two water molecules H-bonded at two *trans*-corner positions of the square tetramer. The donor−acceptor distances for the H-bonds between the water molecules in the hexamer are

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[11] Magnetic susceptibility measurements of solutions were made at 298 K using a Sherwood Scientific magnetic susceptibility balance. Its sensitivity for this purpose, checked using copper sulphate and cobalt chloride solutions, was found to be adequate. The volume of solution used was typically 0.03 mL, and the same volume of distilled water was used as reference to cancel out the diamagnetic effect. A 0.5 M Co^{2+} solution gave a paramagnetic susceptibility of 0.0105 cm^3 mol^{-1} (μ_{eff} = 5.0 μ_B). When mixed with 0.5 M $Ce(NO_3)_6^{4-}$, the measured susceptibility was only 0.002 cm^3 mol^{-1}(of Co^{2+}).

[12] Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988; p 976.

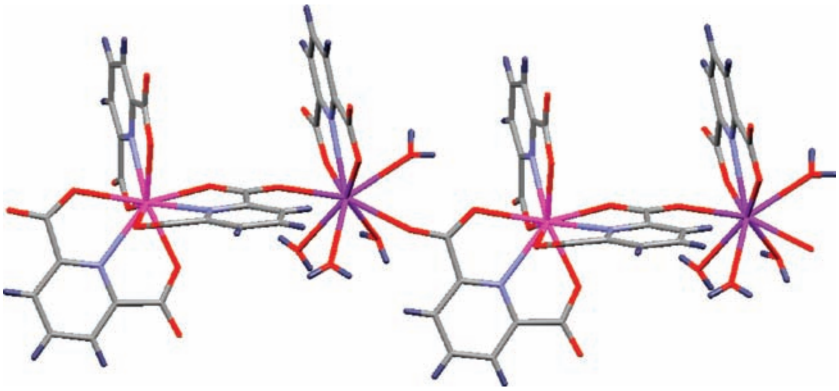

Figure 1. 1D polymeric structure of compound **1**. Disordered and lattice water molecules are omitted for clarity: Ce, purple; La, violet, O, red; N, pale blue; C, gray; and H, dark gray.

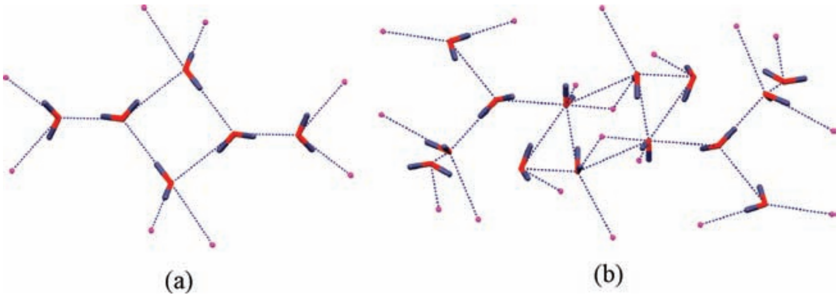

Figure 2. Structure of water clusters: (a) hexamer in compound **1**; (b) 14-mer in compound **4**; O, red; O atoms on the complex, purple; and H, dark gray. Both types of compounds have seven lattice water molecules, only six of which are part of the cluster in **1**.

typically in the range of 2.68−2.96 Å, and the corresponding distances between the hexamer and coordination polymers are in the range of 2.67−2.80 Å. Along with the water hexamer, other water molecules are H-bonded to the carbonyl group of the dipic and coordinated water molecules to form a complicated three-dimensional network.

Structures of [Ln(dipicH)(H_2O)$_6$][Ce(dipic)$_3$]·7H_2O; Ln = Nd (4), Sm(5), Eu (6), Gd (7), or Dy (8). The compounds **4**−**8** have isomorphous ionic structures made up of $[Ln(dipicH)(H_2O)_6]^{2+}$ and $[Ce(dipic)_3]^{2-}$ ions. Both the anion and cation have nine coordinated distorted tricapped trigonal prismatic geometry. The main difference with previous compounds (**1**−**3**) is the coordination of water molecules in place of coordinated carbonyl oxygen on lanthanide atoms which prevents chain formation (Figure 3). $Dipic^{2-}$ and $dipicH^{-}$ ions are present; the acidic hydrogen atom could be located from the difference map. Further, C−O bond length of the carboxyl groups showed significant differences in agreement with protonation. Selected geometrical parameters are given in Tables S9−S13 of the Supporting Information.

In these structures, seven solvent water molecules are present per asymmetric unit, which form a $(H_2O)_{14}$ water cluster (Figure 2b). The water clusters in all compounds have an almost similar structure except that in compounds **5** and **6** one of the solvent water molecules was disordered over two positions. The water clusters have a tetramer core, and two water molecules are H-bonded to two sides of the tetramer, which acts as a bridge between two corners of the tetramer. Two branched chain water tetramers are H-bonded to two opposite corners of the tetramer core. The $(H_2O)_{14}$ cluster is H-bonded to the complex ions to form complex H-bonded networks. The donor−acceptor distances for the H-bonds between the water molecules in the water cluster in these crystals are typically in the range of 2.51−2.97 Å, and the corresponding distances between the cluster and complex ions are in the range of 2.52−3.02 Å.

Structures of [Ln(H_2O)$_7$Ln(dipic)(H_2O)$_4$(Ce(dipic)$_3$)$_2$]$_2$·*n*H_2O; Ln = La (9) *n* = 24, Ce (10) *n* = 24, Pr (11) *n* = 24, or Nd (12) *n* = 26. These structures consist of an octanuclear cluster with a six-membered ring at its core. Crystals of compounds **9**−**11** are isomorphous and contain 24 solvent water molecules per formula unit, while in **12**, there are 26 solvent water molecules. In all compounds, the metal centers have nine-coordinated distorted tricapped trigonal prismatic geometry. The centrosymmetric ring is formed with two units each of $[Ce(dipic)_3]^{2-}$, $[Ln(dipic)(H_2O)_4]^{+}$ and $[Ln(H_2O)_7]^{3+}$ such that each $[Ce(dipic)_3]^{2+}$ is bonded to $[Ln(dipic)(H_2O)_4]^{+}$ and $[Ln(H_2O)_7]^{3+}$ units through the free carbonyl group on each side. Two extra $[Ce(dipic)_3]^{2-}$ units are bonded at both $[Ln(dipic)(H_2O)_4]^{+}$ units on the ring, making it a neutral octanuclear cluster (Figure 4). Selected geometrical parameters are given in Tables S14−S17 of the Supporting Information. No water clusters were observed though a chain of five water molecules exists in all compounds; these and other water molecules are H-bonded to the cluster.

Structures of [(Ln(H_2O)$_5$)$_2$(Ce(dipic)$_3$)$_4$(2H^+)]·*n*H_2O; Ln = Nd (13) *n* = 34, Sm (14) *n* = 26, Eu (15) *n* = 26, or Gd (16) *n* = 26. These structures consist of a hexanuclear cluster with a four-membered ring at its core. Crystals of compounds **14**−**16** are isomorphous and contain 26 solvent water molecules per formula unit, while in **13**, there are 34 solvent water molecules. The

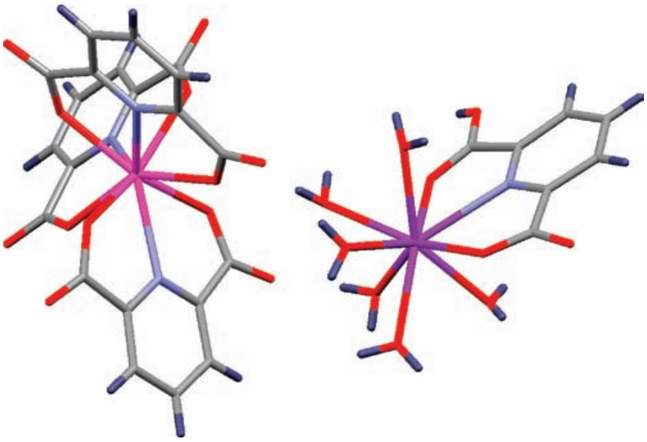

Figure 3. Structure of compound **4**. Lattice water molecules are omitted for clarity: Ce, purple; Nd, violet, O, red; N, pale blue; C, gray; and H, dark gray.

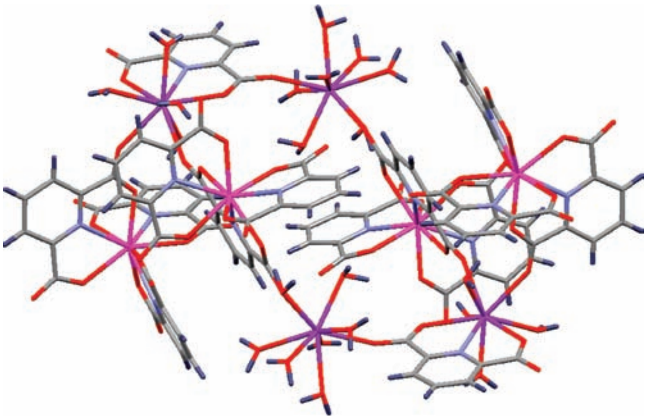

Figure 4. Molecular structure of compound **9**. Lattice water molecules are omitted for clarity: Ce, purple; La, violet, O, red; N, pale blue; C, gray; and H, dark gray.

centrosymmetric ring is formed with two units each of $[Ce(dipic)_3]^{2-}$ and $[Ln(H_2O)_5]^{3+}$ such that each $[Ce(dipic)_3]^{2-}$ is bonded to a $[Ln(H_2O)_5]^{3+}$ unit through the free carbonyl group on each side. An extra $[Ce(dipic)_3]^{2-}$ unit is bonded at each $[Ln(H_2O)_5]^{3+}$ unit on the ring, making it a hexanuclear cluster (Figure 5). All cerium atoms have a tricapped trigonal prismatic coordination, while the Ln^{III} atoms are coordinated in the square antiprismatic mode. If we consider all ligand molecules to be coordinated as $dipic^{2-}$, there will be a net charge of −2 on the cluster, which should be neutralized by protonation of two carboxyl groups of the ligands or two water molecules in the lattice. We were unable to locate these hydrogen atoms from the difference maps. Selected geometric parameters are given in Tables S18−S21 of the Supporting Information.

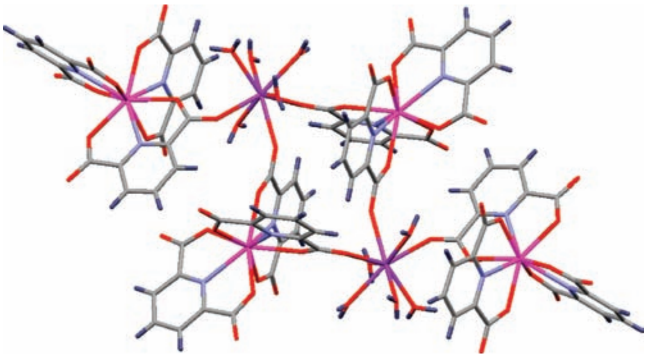

Figure 5. Molecular structure of compound **13**. Lattice water molecules are omitted for clarity: Ce, purple; Nd, violet, O, red; N, pale blue; C, gray; and H, dark gray.

Table 2. Unit Cell Parameters of $[(Ln(H_2O)_5)_2(Ce(dipic)_3)_4(2H^+)]\cdot nH_2O$ (Ln = Tb (**17**), Dy (**18**), Ho (**19**), Er (**20**), Tm (**21**), and Yb (**22**)

	a	*b*	*c*	α	*β*	*γ*	*V*
Tb (**17**)	14.367	15.937	17.299	115.41	113.94	91.97	3163.8
Dy (**18**)	14.367	16.094	17.314	114.22	114.47	91.96	3221.1
Ho (**19**)	14.310	15.664	17.134	114.23	114.10	92.11	3098.9
Er (**20**)	14.317	16.067	17.145	115.13	113.92	92.09	3158.3
Tm (**21**)	14.329	16.125	17.140	115.33	113.70	91.86	3176.1
Yb (**22**)	14.318	15.650	17.123	114.16	114.28	91.59	3100.9

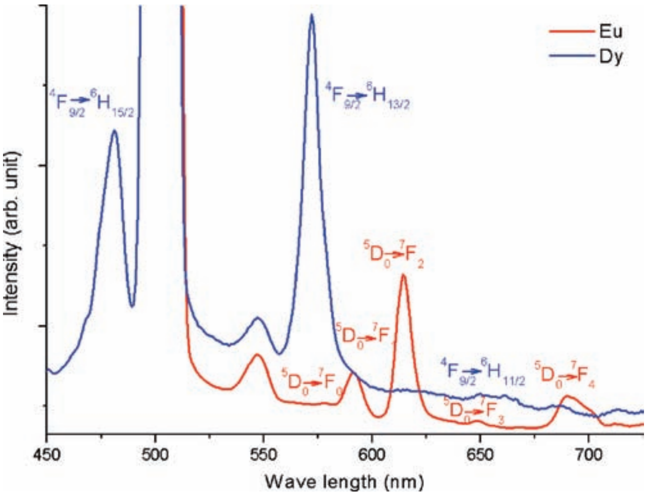

Figure 6. Solid-state luminescence spectra of compound **6** (red) and **8** (blue) excited at 250 nm. The intense band centered at 500 nm is a monochromator artifact.

There are 26 solvent water molecules in compounds **14**, **15**, and **16** and 34 solvent water molecules in **13**. In compound **13**, 26 solvent water molecules form a giant $(H_2O)_{26}$ water cluster that is H-bonded to the complex cluster to form a H-bonded network. The centrosymmetric $(H_2O)_{26}$ water cluster has a chair type hexameric core. Two water dimers are attached at two opposite corners. An irregular water octamer each is fused to two opposite edges (Figure S14 of the Supporting Information). The H-bond contacts between the water molecules in the cluster are in the range of 2.40−2.95 Å and between the cluster and complex cluster molecule they are in the range of 2.66−2.90 Å. In compounds **14**, **15**, and **16**, the solvent water molecules act as bridges between the metal cluster units to form a complex H-bonded network but do not form any water clusters.

Compounds of Other Lanthanides. Compounds of all remaining lanthanides were synthesized (except Pm) by using both molar ratios as that used for the synthesis of the previous compounds, viz., Ln^{III}:Ce^{IV}:dipicH_2, 1:1:3 and 1:1:4. X-ray quality crystals could not be obtained with Lu. Cell parameters of the crystals other than those of Lu were measured at 100 K (Table 2) in order to confirm their isomorphism with the crystals already described. In the case of Dy, the 1:1:3 ratio of the

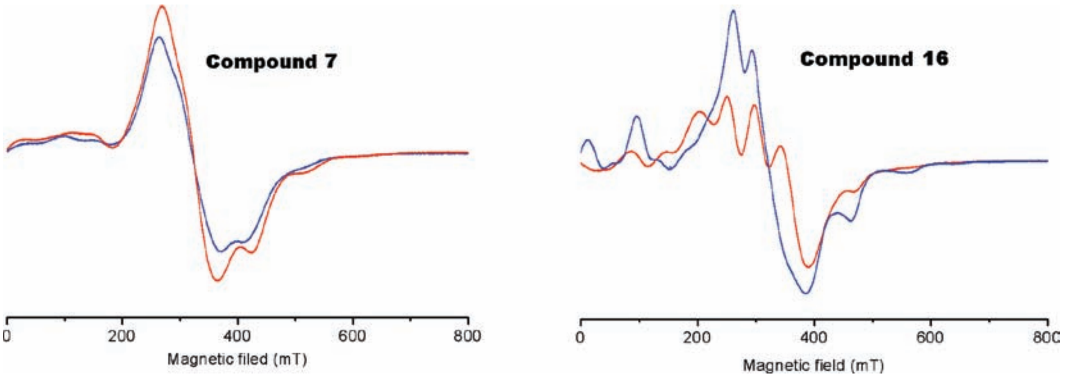

Figure 7. Polycrystalline EPR spectra of compounds **7** and **16** at 300 K (blue) and 120 K (red).

reactants in solution yielded the hexanuclear cluster (analogous to compounds **13**−**16**), while the 1:1:4 ratio had given the ionic salt (compound **8**) as already described. In the case of Tb and heavier elements (Ho, Er, Tm, and Yb), the hexanuclear structure was produced irrespective of the ratio of the reagents in solution. The lutetium compound also in all probability has the same structure, even though it could not be confirmed in the absence of good quality crystal or powder data.

Thermal Analysis. Thermogravimetric data in the temperature range of 25−500 °C at a heating rate of 5 °C/min in a N_2 atmosphere are shown in Figure S19 of the Supporting Information for one compound in each class, viz., 1D-chain (**1**), ionic salt (**4**), octanuclear cluster (**9**), and hexanuclear cluster (**15**). In each case, the loss of water takes place in two stages, a rapid loss to 125 °C and a slow loss to 220 °C. In the case of compounds **4**, **9**, and **15**, the rapid stage itself was completed in two steps, stage-I (to 90 °C) and stage-II (to 125 °C). However, in none of the compounds was there a clear demarcation between solvent and coordinated water. Individual details are as follows. Compound **1**: Total weight loss, 16.6%, including 13% in the rapid stage. Calculated total weight loss for seven solvent (11.1%) and four-coordinated (6.3%) water, 17.4%. Compound **4**: Total weight loss, 19.0%, including 6% in rapid stage-I and 9% in rapid stage-II. Calculated total weight loss for seven solvent (10.7%) and six-coordinated (9.1%) water, 19.8%. Compound **9**: Total weight loss, 19.5%, including 11% in rapid stage-I and 5% in rapid stage-II. Calculated total weight loss for 24 solvent (10.1%) and 22-coordinated (9.3%) water, 19.4%. Compound **15**: Total weight loss, 18.4%, including 6% in rapid stage-I and 9% in rapid stage-II. Calculated total weight loss for 26 solvent (13.4%) and 10-coordinated (5.1%) water, 18.5%. For all four compounds, another weight loss was observed above 250 °C, and the compounds decomposed completely above 420 °C.

Electronic Spectra. Because f−f electronic transitions are inner shell transitions, the ligand field effect will be negligible and normally the electronic spectra observed are those of free ions. Solid-state diffuse reflectance spectra of all compounds were measured (Figure S20, S21 of the Supporting Information) and all show typical lanthanide ion spectra.[13] Virtually identical spectra are obtained for different structures containing the same Ln^{III} ion: La (compounds **1**, **9**); Ce (**2**, **10**); Pr (**3**, **11**); Nd (**4**, **12**, **13**); Sm (**5**, **14**); Eu (**6**, **15**); Gd (**7**, **16**); and Dy (**8**). All compounds have broad absorptions in the region of 1400−1700 and 1900−2400 nm. Some of these low energy bands could be vibrational overtones and combination bands of water molecules. In addition to these broad bands, sharp absorptions are seen for Pr (700 and 1000 nm, weak), Nd (500−900 nm), Sm (1100−1700 nm), and Dy (700−1300 nm). Compounds of trivalent La, Ce, Eu, and Gd are virtually transparent in the visible region. An intense absorption was observed in all compounds below 450 nm (not shown in the figures) and is due to the $Ce(dipic)_3^{2-}$ ion present in all compounds, which is strongly absorbing due to ligand-to-metal charge transfer.

Luminescence Spectra. The f−f transitions being Laporte-forbidden have low extinction coefficients so that luminescence from lanthanide ions can only be observed at very high concentration or when directly excited by laser. The problem can be rectified by the use of sensitizing chromophores as coordinating ligands.[1g] These antenna chromophores may absorb energy and transfer it to the lanthanide ion by an intramolecular energy transfer process. The high-energy singlet excited state of the antenna chromophore may undergo intersystem crossing (ISC) to the triplet state, which in turn facilitates the excitation of the metal center, leading to luminescence. In the present compounds, the dipic ions with strong absorption bands in the range of 240−350 nm act as antenna. In all experiments, excitation was carried out at 250 nm, and for confirming the results, excitation was also carried out at 290 nm, which shows similar results without any change in the luminescence intensity. On the basis of the energy difference between ground state and excited state manifolds, a good quantum yield of visible luminescence is expected for Eu^{III}, Tb^{III}, and to a lesser extent Sm^{III} and Dy^{III}. Compounds **6** (Eu) and **8** (Dy) show well-resolved sharp lines characteristic of the (trivalent) metal ions (Figure 6). The assignment of the prominent bands based on the energy level scheme[1g] of Eu^{III} and Dy^{III} are marked on Figure 6. Another compound **15** (Eu), also shows exactly similar but very weak luminescence as compared to that of **6**. The decreased intensity of compound **15** correlates with the absence of dipic chelation to Eu. Probably for the same reason, the Tb-containing compound **17** also shows only very weak luminescence peaks at 470 nm ($^5D_4 \rightarrow {}^7F_6$) and 545 nm

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(13) Yatsimirskii, K. B.; Davidenko, N. K. *Coord. Chem. Rev.* **1979**, *27*, 223.

($^5D_4 \rightarrow {}^7F_5$). Other compounds did not show any metal-centered emission.

EPR Spectra of Gd^{3+} Compounds. EPR spectra of compounds **7** and **16** in polycrystalline form were measured at 300 and 120 K (Figure 7). The spread of the spectra from 0−600 mT is indicative of the superposition of the zero-field effects of the octet spin state on the Zeeman interaction. The observed increase in intensity upon cooling is expected for a paramagnetic substance. For compound **16**, there are significant differences between spectra at the two temperatures. This indicates greater sensitivity of the zero-field terms to temperature for **16** in contrast to compound **7**. No attempt is made here to extract the spin Hamiltonian parameters from the spectra. Nevertheless, it is clear that the EPR spectrum is sensitive to the change in coordination geometry because compound **7** contains nine-coordinate $[Gd(dipicH)(H_2O)_6]^{2+}$, while **16** contains eight-coordinate $Gd(H_2O)_5(O-)_3$, where (O−) indicates a carboxylate oxygen atom of $dipic^{2-}$ chelated to adjacent Ce^{4+} ions.

Conclusion

Four types of complexes are obtained in the $Ln^{III}-Ce^{IV}-dipicH_2$ system. Type-I: one-dimensional coordination chain having alternate Ce^{IV} and Ln^{III} coordination polyhedra, both nine-coordinate, wherein a $[Ce(dipic)_3]^{2-}$ is linked through a free carboxylate oxygen to a $[Ln(dipicH)(H_2O)_4]^{2+}$ ion on either side. Type-II: a coordination salt made up of $[Ln^{III}(dipicH)(H_2O)_6]^{2+}$ and $[Ce(dipic)_3]^{2-}$ ions. Type-III: an octanuclear cluster containing a six-membered coordination ring. The centro-symmetric ring is made up of two $[Ce(dipic)_3\text{-}Ln(H_2O)_4(dipic)\text{-}Ln(H_2O)_7]^{2+}$ fragments. Two $[Ce(dipic)_3]^{2-}$ units are linked to the $[Ln(H_2O)_4(dipic)]^+$ units of the ring making all metal ions nine-coordinate. Type-IV: a hexa-nuclear cluster containing a four-membered coordination ring. The centro-symmetric ring is made up of two $[Ce(dipic)_3\text{-}Ln(H_2O)_5]^+$ fragments. Two $[Ce(dipic)_3]^{2-}$ units are linked to the $[Ln(H_2O)_5]^{3+}$ units giving a coordination number of eight for the Ln^{III} ion and two lattice H^+ ions.

On the basis of the formation of different structures, the lanthanide series (excluding Pm) may be divided into three groups: Group-I, La, Ce, Pr, and Nd; Group-II, Nd, Sm, Eu, Gd, and Dy; and Group-III, Tb, Ho, Er, Tm, Yb, and Lu. The division is according to atomic masses except for the reversal at Dy and Tb. Nd, being borderline, is included in the two groups.

The Group-III lanthanides form only Type-IV compounds, even when excess $dipicH_2$ is used. This is consistent with their smaller ionic radii and their preference for eight coordination. It is true that $Ln(H_2O)_9{}^{3+}$ is known in some crystals even for the heavier lanthanides.[14] However, in such cases the $Ln-OH_2$ bond is greatly lengthened. It is reasonable that the ring structure with short $Ln-(O, OH_2)$ distances would require a coordination number of eight, which is possible only in a Type-IV structure.

Group-II lanthanides form Type-II or Type-IV compounds, depending on the relative amount of $dipicH_2$ present in the crystallizing solution. Group-I lanthanides, however, form Type-I and Type-III compounds, demonstrating their overwhelming preference for nine coordination and moderate affinity for chelation with dipic. The borderline element, Nd, forms a Type-I compound when initially precipitated but reverts to Type-II when recrystallized. This conversion involves the addition of two water molecules at the Ln^{III} site with concomitant breakdown of the polymeric chain. The reverse process of water displacement by ligand is expected to be more facile for Group-II lanthanides than Group-I on the basis of considerations of ionic size. However, in the present case, there are additional factors, viz., formation of a polymeric chain (rather than chelate) and rearrangement of lattice water molecules in the crystal. From ligand-depleted solutions, a Type-III product crystallizes, while a Type-IV compound is obtained from Nd-depleted solutions. Nd is therefore unique in forming all four types of compounds under different conditions. As expected, the average $Nd-OH_2$ bond is shorter at 2.45 Å in the eight-coordinate structure compared to that of 2.51 Å in the nine-coordinated cases.

As observed in other instances,[15] the coordination chain (Type-I) is a kinetically controlled product, while the ionic structure (Type-II) is the thermodynamically stable product. Given the robustness of the $[Ce(dipic)_3]^{2-}$ ion, it is reasonable to expect the Type-II structure in all cases. Formation of a variety of structures, depending on ionic size and solution composition, is intimately related to the incorporation of lattice water in the crystals. It is remarkable that in spite of differences in crystal structures, the stoichiometry with regard to the solvent water remains the same for Type-I and Type-II compounds. However, in the crystals of the chain polymer (Type-I), a water hexamer is formed, while a larger 14-water cluster is supported by the more flexible packing of Type-II compounds (Figure 2). This arrangement in the latter compounds seems to provide additional stability to compensate for the steric crowding due to the presence of six, rather than four, coordinated water molecules on the nine-coordinate Ln^{3+} ions. In the case of the ring compounds (Type-III and Type-IV), the water molecules, though present in a larger number, do not aggregate as clusters except in the case of the Nd (compound **13**). It seems reasonable to conclude that the loss in entropy by ring formation is compensated by distribution of a large number of relatively free water molecules in the lattice. In the case of compound **13**, there are 36 water molecules per formula unit against 26 in the case of other Type-IV compounds. Of these, 26 water molecules are assembled into a giant cluster.

Electronic spectra do not serve to distinguish between different structures because of the low sensitivity of the f−f transitions to the ligand field. However, EPR, especially its temperature dependence, is much more sensitive to the ligand environment as seen in the case of the two Gd compounds. Dipic ligand is a good sensitizer for electronic emission as demonstrated by the luminescence spectra of Eu and Dy compounds. It is seen that direct chelation as opposed to bridging coordination leads to enhanced luminescence.

The present study covers almost the entire series of lanthanide ions, keeping $dipicH_2$ and $Ce(dipic)_3{}^{2-}$ as common factors. A variety of compounds are obtained depending on the Ln^{III} ion and preparation conditions. There seems to

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(14) Cotton, S. *Comprehensive Coordination Chemistry II*; Parkin, G. F., Ed.; Elsevier: Maryland Heights, MO, 2005; Vol. *3*, p 127.

(15) Sailaja, S.; Reddy, K. R.; Rajasekharan, M. V.; Hureau, C.; Riviere, E.; Cano, J.; Girerd, J.-J. *Inorg. Chem.* **2003**, *42*, 180.

be a symbiotic relationship between the lattice water molecules, free as well as aggregated, and the complex moieties that come in a variety of forms. It is customary to attribute the variations to lanthanide contraction. However, the complexity of the observed trends in the present study is a result of the interplay between the gradual variation in ionic size and Lewis acidity with kinetic effects involving solvent water molecules, free as well as aggregated.

Acknowledgment. This work is dedicated to Prof. P. T. Manoharan on the occasion of his 75th birthday. The X-ray data were collected at the diffractometer facility at University of Hyderabad, established by the Department of Science and Technology, Government of India. Solution magnetic susceptibility studies of $Co^{2+}/Ce(NO_3)_6^{2-}/$ dipicH_2 were made by Ms. T. Nagalaxmi and Mr. S. M. Elahi as part of a master's project. This work was supported by CSIR, India. T.K.P. thanks the CSIR for the award of a research fellowship.

Supporting Information Available: X-ray crystallographic data file in CIF format for all compounds, synthetic and experimental data, crystal data tables, thermal ellipsoid plots, selected geometric parameters, unit cell packing, thermogravimetric plots, and electronic absorption spectra. This material is available free of charge via the Internet at http://pubs.acs.org.