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[Ca(dipicH$_2$)(OH$_2$)$_3$][Ce(dipic)$_3$]·5H$_2$O: A One-Dimensional Coordination Polymer with Alternating CeN$_3$O$_6$ and CaNO$_7$ Polyhedra (dipicH$_2$ = Pyridine-2,6-dicarboxylic Acid)

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The reaction of (NH$_4$)$_2$Ce(NO$_3$)$_6$ and CaCl$_2$ with dipicH$_2$ resulted in the title compound (**1**). **1** crystallizes in the triclinic system, space group $P\bar{1}$, with $a = 11.234(2)$ Å, $b = 12.719(4)$ Å, $c = 16.142(4)$ Å, $\alpha = 95.63(2)°$, $\beta = 103.73(2)°$, $\gamma = 113.83(2)°$, and $Z = 2$. The structure consists of Ce(dipic)$_3^{2-}$ and Ca(dipicH$_2$)(OH$_2$)$_3^{2+}$ ions linked by carboxylate groups forming an infinite linear chain having alternating tricapped trigonal prismatic and square antiprismatic polyhedra.

Introduction

Since the discovery of the dipic ligand in a biological system,[1] its coordination chemistry has been extensively investigated. Several modes of coordination are known: O-unidentate[2] dipicH$_2$; O,N-bidentate[3] dipicH; O,N,O-tridentate[2,3b,4] dipicH$_2$, dipicH, and dipic; (O,N)O-bidentate bridging[5] dipic; (O,N,O)O- and O,N,μ-O-tridentate bridging[4k−l,6] dipic. There has been renewed interest in the complexes of this ligand from several standpoints including unconventional physical properties such as liquid crystal behavior and nonlinear optics,[3b,5b] DNA cleavage,[7] electron transfer,[8] activation of dioxygen,[9] and novel coordination modes.[5b] In the early 1970s, Albertson[6a−d] had reported several complexes of this ligand containing a trivalent lanthanide ion and Na$^+$. Mononuclear and three-dimensional polymeric networks were observed in these compounds. A linear chain structure involving alternating coordinate and H-bond bridges was found[6c] for Na$_3$Yb(dipic)$_3$·NaClO$_4$·10H$_2$O. However, there has been no report of a full coordinatively bridged infinite linear chain involving this ligand. Such structures coupled with proper space group symmetry have the

Table 1. Crystallographic Data for **1**

formula	C$_{28}$H$_{30}$CaCeN$_4$O$_{24}$
fw	986.76
a (Å)	11.234(2)
b (Å)	12.719(4)
c (Å)	16.142(4)
α (deg)	95.63(2)
β (deg)	103.73(2)
γ (deg)	113.83(2)
V (Å^3)	2000.1(8)
Z	2
space group	$P\bar{1}$ (No. 2)
T (°C)	20
λ (Å)	0.71073
ρ_{calcd} (g cm^{-3})	1.638
μ (cm^{-1})	13.59
R1^a	0.038
wR2^b	0.120

^{a} $\mathrm{R1} = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $\mathrm{wR2} = [\sum\{w(F_o^2 - F_c^2)^2\}/\sum(wF_o^4)]^{1/2}$. $w^{-1} = [\sigma^2(F_o^2) + (0.0786P)^2 + 4.13P]$. $P = (F_o^2 + 2F_c^2)/3$.

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**[a]

Ce Coordination

Bond Distances

Ce−O3	2.330(3)	Ce−O1	2.341(3)
Ce−O5	2.341(3)	Ce−O7	2.353(3)
Ce−O11	2.378(3)	Ce−O9	2.388(3)
Ce−N1	2.516(3)	Ce−N2	2.522(3)
Ce−N3	2.526(4)		

Bond Angles

O3−Ce−O1	127.48(11)	O3−Ce−O5	80.45(12)
O1−Ce−O5	86.25(12)	O3−Ce−O7	144.18(12)
O1−Ce−O7	81.52(11)	O5−Ce−O7	127.03(11)
O3−Ce−O11	87.73(12)	O1−Ce−O1	176.84(12)
O5−Ce−O11	147.14(12)	O7−Ce−O1	178.48(12)
O3−Ce−O9	76.36(11)	O1−Ce−O9	149.87(11)
O5−Ce−O9	79.65(11)	O7−Ce−O9	85.93(11)
O11−Ce−O9	127.20(11)	O3−Ce−N1	63.83(11)
O1−Ce−N1	63.65(11)	O5−Ce−N1	74.57(11)
O7−Ce−N1	138.66(12)	O11−Ce−N1	72.70(12)
O9−Ce−N1	135.25(11)	O3−Ce−N2	137.06(12)
O1−Ce−N2	75.07(11)	O5−Ce−N2	63.60(11)
O7−Ce−N2	63.44(12)	O11−Ce−N2	135.18(12)
O9−Ce−N2	74.81(11)	N1−Ce−N2	122.14(11)
O3−Ce−N3	73.39(12)	O1−Ce−N3	134.88(12)
O5−Ce−N3	138.87(12)	O7−Ce−N3	70.87(12)
O11−Ce−N3	63.39(12)	O9−Ce−N3	63.83(11)
N1−Ce−N3	118.59(11)	N2−Ce−N3	119.24(12)

Ca Coordination

Bond Distances

Ca−O2	2.429(3)	Ca−OW3	2.400(5)
Ca−OW2	2.407(5)	Ca−O10#1	2.429(4)
Ca−OW1	2.470(4)	Ca−O13	2.501(4)
Ca−N4	2.537(4)	Ca−O15	2.575(4)

Bond Angles

OW3−Ca−OW2	79.8(2)	OW3−Ca−O2	73.0(2)
OW2−Ca−O2	100.7(2)	OW3−Ca−O10#1	74.4(2)
OW2−Ca−O10#1	87.1(2)	O2−Ca−O10#1	144.51(12)
OW3−Ca−OW1	142.4(2)	OW2−Ca−OW1	83.5(2)
O2−Ca−OW1	143.66(14)	O10#1−Ca−OW1	71.24(13)
OW3−Ca−O13	81.9(2)	OW2−Ca−O13	157.1(2)
O2−Ca−O13	86.96(12)	O10#1−Ca−O13	74.71(14)
OW1−Ca−O13	103.2(2)	OW3−Ca−N4	134.4(2)
OW2−Ca−N4	139.1(2)	O2−Ca−N4	76.12(12)
O10#1−Ca−N4	119.40(14)	OW1−Ca−N4	77.6(2)
O13−Ca−N4	63.64(12)	OW3−Ca−O15	135.1(2)
OW2−Ca−O15	76.9(2)	O2−Ca−O15	74.28(12)
O10#1−Ca−O15	140.84(13)	OW1−Ca−O15	71.57(13)
O13−Ca−O15	126.04(12)	N4−Ca−O15	62.85(11)

COOH Groups

Bond Distances

C22−O13	1.236(6)	C22−O14	1.288(6)
C28−O15	1.204(6)	C28−O16	1.313(6)

Bond Angles

O13−C22−O14	125.1(5)	O15−C28−O16	125.3(5)

[a] Symmetry transformation used to generate equivalent atoms: (#1) $x - 1, y - 1, z$.

potential for solid-state applications.[10] The use of Ce^{4+} and Ca^{2+} allows the preparation of a 1:1 complex with a linear polymeric structure reported in this paper.

Experimental Section

All chemicals used were of reagent grade. DipicH_2 was bought from Fluka Chemicals.

[Ca(dipicH$_2$)(OH$_2$)$_3$][Ce(dipic)$_3$]·5H$_2$O (1). $(NH_4)_2Ce(NO_3)_6$ (548 mg, 1.02 mmol) and $CaCl_2$ (110 mg, 0.99 mmol) were dissolved in 4 mL of water. To this, a solution of dipicH_2 (668 mg, 4.00 mmol) in 40 mL of methanol was added slowly, with stirring. The solution changed from orange to bright red and finally to light yellow. After being stirred for a while, the solution yielded a light yellow precipitate. It was filtered off, washed successively with water and methanol, and dried. Yield: 0.846 g (0.86 mmol, 86%). Recrystallization by slow evaporation of an aqueous solution gave rhombus-shaped light yellow crystals suitable for X-ray work. Anal. Calcd for $CeCaC_{28}H_{30}N_4O_{24}$: C, 34.08; H, 3.06; N, 5.68; Ca, 4.06; Ce, 14.20. Found: C, 34.89; H, 2.67; N, 6.36; Ca, 3.92 (by atomic absorption spectrometry); Ce, 14.50 (by iodometry). IR (KBr disk, cm^{-1}): 3474 (b), 1641 (C═O), 1427, 1367 (b), 1265, 1184, 1076, 1024, 923, 769,734, 688, 665, 578.

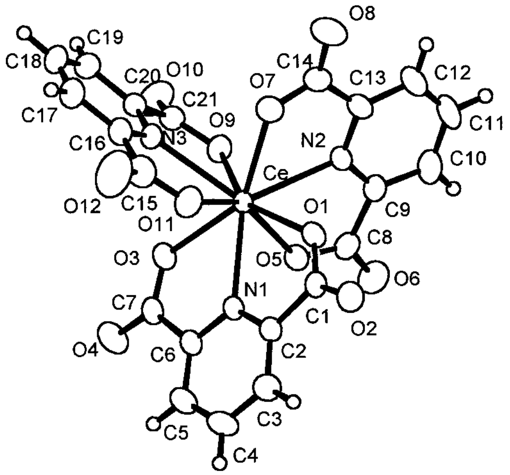

Figure 1. Structure of Ce(dipic)$_3^{2-}$ in **1**. Atoms are represented by displacement ellipsoids at 50% probability levels.

X-ray Crystallography. X-ray data were collected using graphite monochromated Mo Kα radiation on an Enraf-Nonius CAD4 diffractometer for a crystal with dimensions of 0.35 × 0.20 × 0.15 mm. An empirical absorption correction based on a ψ-plot[11a] was applied to the intensity data. The crystal belongs to the triclinic system. The structure was solved (SHELXS-86[11b]) and refined (over F^2, SHELXL-93[11c]) in the $P\bar{1}$ space group. All non-hydrogen atoms were refined anisotropically. Among the five lattice water molecules, three were found to be in great disorder. The ring hydrogens were assigned positions on the basis of geometrical considerations and were allowed to ride upon the respective carbon atoms. The hydrogen atoms of the carboxylic groups and the coordinated water molecules as well as two of the lattice water molecules were located in difference maps, and their positions were refined. Bond length constraints were applied to the water hydrogens. The final R1 and wR2 values were 0.0376 and 0.1196, respectively for reflections with $I > 2\sigma(I)$. Crystal data are given in Table 1 and selected bond lengths and angles in Table 2.

Results and Discussion

Solution Chemistry. The complex was obtained in good yield when Ce^{4+}, Ca^{2+}, and dipicH_2 were mixed in a 1:1:4 ratio. While the alcoholic dipicH_2 was being added, there was a change in color from orange to bright red and finally to light yellow. However, in the absence of Ca^{2+}, the color of the solution changes from orange to red, and remains so. After keeping this solution in a desiccator over H_2SO_4 for 3−4 days, large dark brownish crystals formed. These, highly efflorescent crystals are probably the ammonium salt of Ce(dipic)$_3^{2-}$. Hence, it appears that the polymer is formed by the reaction of Ca^{2+} with the Ce(dipic)$_3^{2-}$ ion in the presence of excess dipicH_2. The polymer is moderately soluble in water and in dmf, resulting in a clear yellow solution. It was possible to neutralize the

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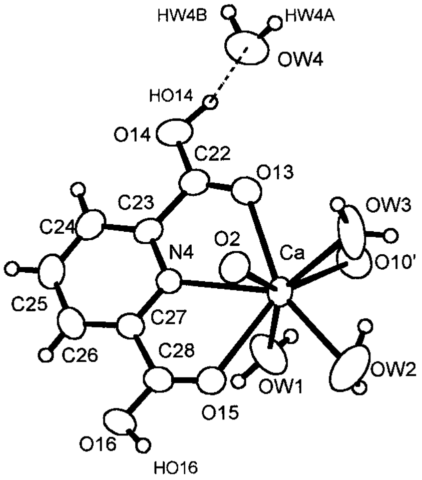

Figure 2. Structure of Ca $(dipicH_2)(OH_2)_3^{2+}$ in **1**. Atoms are represented by displacement ellipsoids at 50% probability levels.

aqueous solution by 2 equiv of NaOH solution from which yellow crystals were obtained. On the basis of iodometric titration, an empirical formula of $Na_2Ce(dipic)_3$ was deduced for these crystals, instead of the anticipated Na salt of the linear chain. So, it is evident that the polymer is stable only in acidic medium and dissociates even at neutral pH.

Structure. Three tridentate $dipic^{2-}$ ligands coordinate to Ce^{4+} in a slightly distorted tricapped trigonal prismatic mode (Figure 1). A tridentate $dipicH_2$ and three water molecules are bound to Ca^{2+}. The protonated ligand is bound through the two carbonyl oxygen atoms and the ring nitrogen atom. Two of the $dipic^{2-}$ ligands on Ce^{4+} act as a bridge with two different Ca^{2+} ions, thus completing a distorted square antiprismatic type of eight-coordination around each Ca^{2+} ion (Figure 2). The resulting structure is an infinite linear chain made up of alternating Ce and Ca polyhedra (Figure 3). The Ce−Ca distance alternates between 6.409(2) and 6.831(2) Å along the chain. One of the lattice water molecules forms a strong H-bond (HO14···OW4 = 1.47(9) Å, OW4···HO14···O14 = 164(7)°) with a COOH group of $dipicH_2$. This makes the two COOH groups have appreciably different bond distances (Table 2). Such differences between the two carboxylic groups of $dipicH_2$ bound to several metal ions such as Pb^{2+},[6g] Cu^{2+},[4d] Ag^{2+},[4a] and Na^{+},[2] are known in the literature. The ligand itself crystallizes as a monohydrate with the water molecule H-bonded to one of the COOH groups.[12]

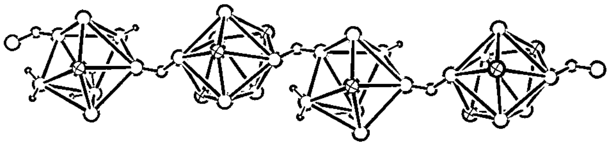

Figure 3. A perspective view of a segment of the polymeric chain formed by the linking of coordination polyhedra in **1**. Three dipic nitrogen atoms cap the trigonal prism formed by the carboxylate oxygen atoms (large open circles) around cerium. The square antiprism around calcium is formed by three water molecules, one dipicH2 nitrogen atom, and four carboxylate oxygen atoms. The alternating $CaNO_7$ and CeN_3O_6 polyhedra are linked by carboxylate groups (C1 and C21, small open circles). The Ca and Ce atoms are not shown.

While there is no previous report of a dipic complex of Ce(IV), $Na_3Ce(III)(dipic)_3\cdot 15H_2O$ was found[6d] to be isomorphous with the Nd complex,[6d] which has tricapped trigonal prismatic $Nd(dipic)_3^{3-}$ ions linked to form a three-dimensional network involving Na^{+}, carboxylate groups, and lattice water. Ca^{2+} forms a dinuclear complex $[Ca(dipic)(OH_2)_3]_2$,[6e] in which Ca^{2+} is seven coordinate. A triiron linear chain is observed[4k] in Fe_3^{II} $(dipic)_2(dipicH)_2(OH_2)_4$, in which a central $Fe(OH)_4^{2+}$ unit is linked to two $Fe(dipicH)(dipic)^{-}$ units via carboxylate bridges.

Conclusion

The well-known geometries for eight and nine coordination, namely, square antiprism and tricapped trigonal prism, are present together in **1**. The formation of a linear chain of cation and anion polyhedra with the interionic separation alternating between 6.4 and 6.8 Å is important in the context of second harmonic generation.[10] However, such an application would require a non-centrosymmetric polymorph or solvate of **1** or a similar compounds with other M^{2+} ions.

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Supporting Information Available: One crystallographic file, in CIF format, is available on the Internet only. Access information is given on any current masthead page.

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