Polyhedron 62 (2013) 83–88

Contents lists available at SciVerse ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Lanthanide coordination polymers with bis(diphenylphosphoryl)bicyclo[1.1.1]pentane

Zdenek Spichal, Andrej Jancarik, Ctibor Mazal, Jiri Pinkas, Pavla Pekarkova, Marek Necas *

Department of Chemistry, Faculty of Science, Masaryk University, Kotlarska 2, 611 37 Brno, Czech Republic
CEITEC – Central European Institute of Technology, Masaryk University, Kamenice 5, 625 00 Brno-Bohunice, Czech Republic

ARTICLE INFO

Article history:
Received 7 April 2013
Accepted 16 June 2013
Available online 27 June 2013

Keywords:
Bicyclopentanes
Lanthanides
Coordination polymers
X-ray crystallography

ABSTRACT

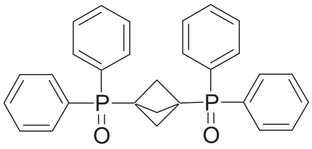
The reaction of 1,3-bis(diphenylphosphoryl)bicyclo[1.1.1]pentane (**1**) with lanthanide nitrates provided a series of layered network coordination polymers $Ln(\mathbf{1})_{1.5}(NO_3)_3$ (Ln = Ce, Pr, Nd, Eu, Tb, Er, Yb, Lu). Crystal structures of all members of the series were determined by single crystal X-ray diffraction and were found isostructural. The compounds were studied by IR spectroscopy, luminescence spectroscopy, thermal analysis (TG/DSC) and powder X-ray diffraction (PXRD) techniques.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Recently we have introduced a series of polymeric complexes with bidentate diphosphine dioxide ligands $Ph_2P(O)–X–P(O)Ph_2$, with both flexible [$X = (CH_2)_2$, $(CH_2)_6$] [1,2] and rigid [$X = C_6H_4$] [3] central backbones. Depending on the experimental conditions and the size of the lanthanide ions, several types of coordination polyhedra and layered network or one-dimensional architectures were detected in the crystal structures of the complexes. The compounds with 1,2-bis(diphenylphosphoryl)ethane were polymers which possessed parquet-floor, brick-wall and honeycomb architectures with a 2:3 metal-to-ligand ratio. The reactions of lanthanide ions with 1,6-bis(diphenylphosphoryl)hexane yielded square-grid layer network polymers with the metal-to-ligand ratio increased to 1:2. Finally, 1,4-bis(diphenylphosphoryl)benzene afforded one-dimensional coordination polymers based on a 2:3 metal-to-ligand ratio.

For further studies, we have chosen another rigid backbone spacer, 1,3-bis(diphenylphosphoryl)bicyclo[1.1.1]pentane (**1**). The central part of **1**, the bicyclopentane cage, is known as a strained but kinetically stable building block. Its collinear pair of bridgeheadexocyclic bonds makes it an attractive straightforward rigid σ-bonded non-conjugated spacer/linker in a modular construction set for nanotechnology [4]. It can be functionalized at the bridgehead positions in a variety of ways; several derivatives have been used as ligands in complexes with d-block metals [5–8]; however, none of those complexes has been found to be polymeric.



1

Encouraged by the successful preparation of the polymeric lanthanide complexes with diphosphine dioxide ligands, we have reacted lanthanide nitrates with **1**. The crystal structures of eight resulting compounds ($(Ln(\mathbf{1})_{1.5}(NO_3)_3$ = **1Ce**, **1Pr**, **1Nd**, **1Eu**, **1Tb**, **1Er**, **1Yb**, **1Lu**) were established by single crystal X-ray diffraction and their properties were characterized by IR spectroscopy, and thermal analysis (TG/DSC) techniques (Table 1). For the europium polymer, excitation and emission spectra were measured, and the luminescence lifetimes in solid state and acetonitrile were determined.

2. Results and discussion

The ligand **1** was prepared according to Scheme 1 by reaction of chlorodiphenylphosphine with bicyclo[1.1.1]pentane-1,3-diide dianion [9], which was generated from [1.1.1]propellane (**2**) [10,11] by a reduction with 4,4′-di-*tert*-butylbiphenyl (DTBBP) radical anion in dimethyl ether (DME), and subsequent oxidation of the primarily formed diphosphine (**3**).

The polymeric complexes **1Ce** to **1Lu** originated from a self-assembly of **1** with lanthanide cations in simple precipitation

---

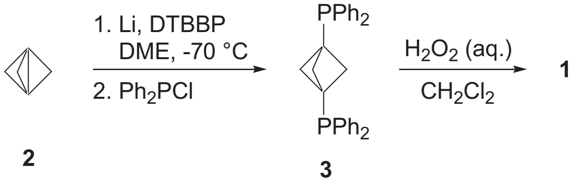
* Corresponding author. Tel.: +420 549496060.
E-mail address: man@chemi.muni.cz (M. Necas).

0277-5387/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.poly.2013.06.026

Table 1
Table of prepared compounds and their characterization.

	Formula	Yield		Analyses C, H, N (%)		Selected IR band (cm^{-1})
		(mg)	(%)	Found[b]	Required	
1Ce	Ce$(C_{29}H_{26}P_2O_2)_{1.5}(NO_3)_3$	36	49	50.19, 3.79, 4.02	50.78, 3.82, 4.08	ν(PO) 1150, $\nu(NO_3)$ 1481, 1302, 1292, 1028
1Pr	Pr$(C_{29}H_{26}P_2O_2)_{1.5}(NO_3)_3$	54	74	50.41, 3.82, 3.95	50.74, 3.82, 4.08	ν(PO) 1151, $\nu(NO_3)$ 1481, 1304, 1294, 1029
1Nd	Nd$(C_{29}H_{26}P_2O_2)_{1.5}(NO_3)_3$	–[a]	–[a]	49.82, 3.79, 3.93	50.58, 3.81, 4.07	ν(PO) 1153, $\nu(NO_3)$ 1482, 1306, 1295, 1029
1Eu	Eu$(C_{29}H_{26}P_2O_2)_{1.5}(NO_3)_3$	55	75	50.01, 3.77, 3.94	50.21, 3.78, 4.04	ν(PO) 1156, $\nu(NO_3)$ 1483, 1312, 1300, 1031
1Tb	Tb$(C_{29}H_{26}P_2O_2)_{1.5}(NO_3)_3$	32	43	49.51, 3.74, 3.97	49.87, 3.75, 4.01	ν(PO) 1159, $\nu(NO_3)$ 1481, 1315, 1302, 1032
1Er	Er$(C_{29}H_{26}P_2O_2)_{1.5}(NO_3)_3$	38	51	49.15, 3.71, 3.84	49.48, 3.72, 3.98	ν(PO) 1162, $\nu(NO_3)$ 1482, 1320, 1303, 1034
1Yb	Yb$(C_{29}H_{26}P_2O_2)_{1.5}(NO_3)_3$	56	74	48.95, 3.70, 3.83	49.21, 3.70, 3.96	ν(PO) 1161, $\nu(NO_3)$ 1483, 1323, 1304, 1035
1Lu	Lu$(C_{29}H_{26}P_2O_2)_{1.5}(NO_3)_3$	33	44	48.57, 3.65, 3.77	49.12, 3.70, 3.95	ν(PO) 1162, $\nu(NO_3)$ 1483, 1324, 1305, 1036

[a] Remaining ligand (<15 mg) was used for the reaction; the yield and TG/DSC data were not determined.
[b] Methanol residues (confirmed in crystals by X-ray diffraction) may be responsible for lower *C* values in some samples.



Scheme 1.

reactions. The methanolic solutions of the ligand and the respective lanthanide nitrate were put together without subsequent stirring and single crystals started to form after ca. 30 min. If the reaction mixture was stirred, the microcrystalline product precipitated within a few seconds.

The polymeric complexes **1Ce** to **1Lu** are isostructural in the solid state (Table 2). Their 2D networks are built in a similar manner like those in coordination polymers of Pr and Nd with 1,2-bis(diphenylphosphoryl)ethane (**4**), **4Pr** and **4Nd**, respectively [1]. They all show parquet-floor architectures based on the (6,3) topology (Fig. 1). Although the solid state structure of the free ligand **1** is not known, the average P···P intramolecular distance in **1Nd** is 5.480 Å while 4.416 Å was found for **4** in **4Nd**. Consequently, the tile dimensions defined by Nd–Nd separations are 10.2×19.5 Å^2 in **1Nd** while in **4Nd** are 9.3×17.1 Å^2. A side view of the network layers reveals their highly undulating nature allowing a convenient accommodation of phenyl moieties on phosphorus atoms. The "height" of such a wave measured as the distance between the plane of the lanthanide atoms in the "wave trough" and the plane of the lanthanide atoms in the "wave crest" is 5.816 Å in **1Nd**. The corresponding value observed for **4Nd** is lower (5.354 Å), as expected for the shorter spacer.

It is worth noting that the polymers of **4** show several architectures, although their metal-to-ligand stoichiometric ratio and topology is constant throughout the lanthanide series. While for the lighter lanthanides the parquet-floor motif was observed, the heavier metals adopted brick-wall architectures; with Lu, only a binuclear complex was isolated. Moreover, using another synthetic approach, honeycomb networks were obtained with Pr and Nd. Witnessing the architectural consistency of the present complexes, we conclude that this is owing to the rigid nature of **1** which directs a process of self-assembly towards uniform metal-organic frameworks regardless of the size of the cations.

The bond lengths and angles for the present complexes are listed in Table 3. If nitrate groups are considered as pseudomonodentate ligands, the coordination polyhedra LnO_3N_3 are distorted octahedral, with meridional arrangement of the donor atoms (Fig. 2). As typical for lanthanide nitrate complexes with mono- and polydentate tertiary phosphine oxides, the Ln–O(P) bonds are consistently shorter than the Ln–O(N) bonds along the **1Ce** to **1Lu** series. It has been pointed out [12] that the decrease in the Ln–O distances from Ce to Lu can be ascribed exclusively to the lanthanide contraction if the respective ionic radii are subtracted from the Ln–O distances and the resulting values are approximately constant. For the present compounds, we have found that the average Ln–O(P) distances adjusted for the decrease in ionic radii vary from 1.05 to 1.06 Å, while the adjusted average Ln–O(N) distances vary from 1.25 to 1.27 Å (excluding Ln–O bonds to disordered nitrate groups); therefore, the lanthanide contraction seems to be the only factor affecting the Ln–O distances from **1Ce** to **1Lu**. The *mer*-pseudooctahedral polyhedra naturally involve two types of nitrate ligands; those mutually *trans* and those *trans* to P═O groups. The lanthanide contraction may also influence their conformation in a sterically strained environment, as shown in a recent study of the $Ln(NO_3)_3(^iBu_3PO)_3$ complexes featuring an analogous coordination geometry [13]. For heavier lanthanides starting with Sm, significant lowering of *cis* N–Ln–N angles and dihedral angles between the planes of the mutually *trans* nitrate groups was observed. This closing of the angles relates to a release of the steric strain introduced mainly by bulky organic moieties of $^iBu_3PO$. In the present complexes, no abrupt changes in the ligand positioning are apparent across the lanthanide series. The *cis* N–Ln–N angles range from 86.54° to 89.70° and the dihedral angles between the planes of the *trans* positioned nitrate ligands vary from 87.20° to 89.87°. We can thus conclude that in comparison with $^iBu_3PO$ the ligand **1** has lower steric requirements for which the coordination sphere of smaller lanthanides does not need to be adapted. The mutually *trans* nitrate ligands are coordinated in a slightly asymmetric manner, showing the average difference in Ln–O bond lengths of 0.046 Å. The Ln–O–P angles adopt the values between 160.07(10)° and 172.77(14)° and more or less approach a linearity which is characteristic for non-directional electrostatic lanthanide bonding.

The infrared spectra of the complexes are dominated by prominent bands corresponding to P═O (1150 to 1162 cm^{-1}) stretching frequencies (Table 1). The presence of bidentate nitrate groups is shown as strong absorptions at 1471–1507 and 1292–1324 cm^{-1} which are attributed to ν(N═O) and $\nu_a(NO_2)$, respectively [14]. The latter region of the spectra in particular is clearly distinguished into two bands for heavier lanthanides (Tb–Lu). A weak band at 1028–1036 cm^{-1} is assigned to $\nu_s(NO_2)$. Almost negligible absorption in the region of OH stretching vibrations confirmed only a little or no presence of a solvent.

Thermal analysis (TG/DSC) experiments were performed to establish the stability of coordination polymers (Table 4, Fig. 3). The studied complexes were stable on heating up to 340–350 °C with the exception of **1Ce** which decomposed already at 324 °C. The first precipitous mass decrease (Step I in Table 4) is accompanied by a strong exothermic effect with a maximum at 354–360 °C. This mass loss can be attributed to the nitrate decomposition and

Download English Version:

https://daneshyari.com/en/article/1337193

Download Persian Version:

https://daneshyari.com/article/1337193

Daneshyari.com