This article was downloaded by:
On: *24 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Synthesis and Spectral Investigation of La(III), Ce(III), Pr(III), Nd(III) and Sm(III) Coordination Chain Polymeric Assemblies

N. H. Patel[a]; P. K. Panchal[a]; P. B. Pansuriya[a]; M. N. Patel[a]
[a] Department of Chemistry, Sardar Patel University, Gujarat, India

To cite this Article Patel, N. H. , Panchal, P. K. , Pansuriya, P. B. and Patel, M. N.(2006) 'Synthesis and Spectral Investigation of La(III), Ce(III), Pr(III), Nd(III) and Sm(III) Coordination Chain Polymeric Assemblies', Journal of Macromolecular Science, Part A, 43: 7, 1083 — 1090

To link to this Article: DOI: 10.1080/10601320600740306

URL: http://dx.doi.org/10.1080/10601320600740306

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Journal of Macromolecular Science®, Part A: Pure and Applied Chemistry, 43:1083–1090, 2006
Copyright © Taylor & Francis Group, LLC
ISSN 1060-1325 print/1520-5738 online
DOI: 10.1080/10601320600740306

Synthesis and Spectral Investigation of La(III), Ce(III), Pr(III), Nd(III) and Sm(III) Coordination Chain Polymeric Assemblies

N. H. PATEL, P. K. PANCHAL, P. B. PANSURIYA, AND M. N. PATEL

Department of Chemistry, Sardar Patel University, Gujarat, India

Downloaded At: 10:47 24 January 2011

The coordination chain polymers of La(III), Ce(III), Pr(III), Sm(III) and Nd(III) with N,N′-di(o-carboxyphenyl)terephthalaldehydediimine have been prepared. The characterization of these newly synthesized coordination chain polymers were done by elemental analysis, magnetic measurements, infrared spectra, reflectance spectral studies and thermogravimetric analysis. The Schiff base acts as a dinegative tetradentate ligand and bonding through the oxygen and nitrogen atoms. The insolubility of the coordination chain polymers in common organic solvents suggest their polymeric nature.

Keywords Schiff base, polymeric assemblies, thermally stable, spectral investigation

Introduction

The coordination chemistry of f-block elements is an active area of the research (1). The complexes of lanthanide ions with Schiff bases have been reported (2, 3). Coordination polymer and 0D frameworks, built up of metal centers linked organic ligands, have been extensively studied in recent years with especial interest in their utility for molecular recognition, non-linear optical properties or for catalytic purposes (4). Lanthanide coordination polymers have opened up a large number of opportunities in growing fields of large social and economical impact, such as environmental sciences, medical diagnostics, luminescent material due to its electronic and/or photochemical nature of organic-inorganic hybrid copolymer with covalent bonding, and cell biology (5–7). Chelating polymers are more interesting due to their applications in waste water treatment, metal recovery from diluted solutions as protective coatings on metal surfaces or as a priming layer, coating on paper, fiber as fabric, selective binding of enzymes (8). These types of polymers are less common. In fact, lanthanide ion possesses a diverse coordination-mode and a variable coordination number, which would be used to furnish a high-dimension coordination polymer as nodes (9), high coordination number of lanthanide ions in lanthanide coordination polymers are reported (10, 11). In continuation of earlier work (12), we prepared N,N′-di(*o*-carboxyphenyl)-terephathalaldehydediimine, which

Received November 2005; Accepted January 2006.

Address correspondence to M. N. Patel, Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar-388 120, Gujarat, India. Tel.: 91 2692 226857; E-mail: jeenenpatel@yahoo.co.in

react with lanthanide metal ions like La(III), Ce(III), Pr(III), Nd(III) and Sm(III). The coordination polymers were characterized on the basis of elemental analysis, infrared spectra, electronic spectra, magnetic measurements and thermogravimetric measurements. A suggested structure of the ligand is shown in Figure 1.

Experimental

Methods and Materials

Preparation of Schiff Base. All the chemicals used were of analytical grade and used without further purification. The ethanolic solution (100 mL) of terephthalaldehyde (1.34 g, 1 mmol) and *o*-aminobenzoic acid (2.74 g, 2 mmol) were mixed and a yellow crystalline solid was obtained immediately. The mixture was heated in a water bath for 1 h. The ligand was filtered, washed successively with water and ethanol, and dried in air. It is insoluble in common organic solvents, like benzene, chloroform, and acetone, but soluble in dimethyl formamide.

Preparation of Coordination Polymers. The solution (100 mL) of metal nitrate (2 mmol) in dimethyl formamide was slowly added to a dimethyl formamide solution of the ligand (0.6 g, 2 mmol) in 1 : 1 mole ratio. The mixture was heated for 10 h at 120°C to ensure complete precipitation and then allowed to cool overnight at room temperature. The obtained coordination polymer was filtered, washed with dimethyl formamide and dried in air. The coordination polymers are insoluble in all common organic solvents like acetone, ethanol, chloroform, methanol, benzene, dimethyl formamide, etc.

Downloaded At: 10:47 24 January 2011

Analytical Procedure

The coordination polymers were analyzed for the metal contents by the EDTA titration technique (13). The magnetic moment has been obtained by Gouy's method using mercury tetrathiocyanato cobaltate(II) as a calibrant ($\chi_g = 16.44 \times 10^{-6}$ c.g.s. unit at 20°C.). Diamagnetic corrections were made using Pascal's constant. Infrared spectra were measured on a FT-IR Nicolet 400D spectrophotometer in KBr pellets. The electronic spectra were measured on a Beckman DK-2A spectrophotometer using MgO as a reference. The nitrogen, carbon and hydrogen were analyzed with a model 240 Perkin-Elmer elemental analyzer.

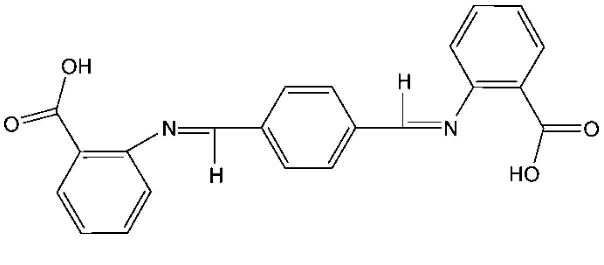

Figure 1. Suggested structure of the ligand (H_2SB).

Downloaded At: 10:47 24 January 2011

Table 1
Analytical data of the coordination polymers

Compound empirical formula	Formula weight	Yield %	% Found (calcd.)				M. p. °C	$\mu_{eff.}$ B.M.
			M	C	H	N		
H_2SB $C_{22}H_{16}N_2O_4$	372.0	80	—	70.90 (70.92)	4.28 (4.30)	7.49 (7.52)	114	—
$[La(SB)(H_2O)(NO_3)]_n \cdot H_2O$ $C_{22}H_{18}LaN_3O_9$	606.9	40	22.90 (22.88)	43.50 (43.49)	2.95 (2.96)	6.95 (6.92)	>360	—
$[Ce(SB)(H_2O)(NO_3)]_n \cdot H_2O$ $C_{22}H_{18}CeN_3O_9$	608.1	45	23.00 (23.03)	43.44 (43.41)	2.98 (2.90)	6.92 (6.90)	>350	2.30
$[Pr(SB)(H_2O)(NO_3)]_n \cdot H_2O$ $C_{22}H_{18}PrN_3O_9$	608.9	38	23.11 (23.14)	43.50 (43.47)	2.93 (2.95)	6.91 (6.89)	>350	3.95
$[Nd(SB)(H_2O)(NO_3)]_n \cdot H_2O$ $C_{22}H_{18}NdN_3O_9$	612.2	50	23.53 (23.55)	42.13 (43.10)	2.92 (2.94)	6.87 (6.86)	>350	3.60
$[Sm(SB)(H_2O)(NO_3)]_n \cdot H_2O$ $C_{22}H_{18}SmN_3O_9$	618.4	48	24.30 (24.32)	42.70 (42.73)	2.90 (2.91)	6.80 (6.79)	>350	2.40

H_2SB = N,N′-di-(*o*-carboxyphenyl)terephthalaldehydediimine.

Results and Discussion

The analytical data and some physical properties are listed in Table 1. The reaction may be represented as follows:

$$M(NO_3)_3 \cdot nH_2O + H_2SB \longrightarrow [MSB(H_2O)NO_3]_n \cdot H_2O + 2HNO_3 + (n-2)H_2O$$

where, M = La(III), Ce(III), Pr(III), Nd(III) and Sm(III); H_2SB = di(*o*-carboxyphenyl)terephthalaldehydediimine.

All the coordination polymers exhibit 1 : 1 metal to ligand stoichiometry. Insolubility of the compounds in almost all the solvents limits the determination of molecular weights. It is suggested that the compounds are coordination chain polymers (12) and suggested structure of the coordination chain polymer is shown in Figure 2.

Magnetic Measurements

The magnetic moment value among the trivalent lanthanide ions is due to the presence of unpaired '4f' electrons. The magnetic measurements were carried out at room temperature and listed in Table 1. The compound of lanthanum(III) shows diamagnetism (14). The compounds of the cerium (2.30 B.M.), prosedymium (3.95 B.M.), neodymium (3.60 B.M.) and samarium (2.42 B.M.) show paramagnetism.

Downloaded At: 10:47 24 January 2011

Infrared Spectra

The spectra of all the coordination polymers show the band about 3400 cm^{-1} due to the presence of coordinated water (15). The ligand shows the ν(C=N) stretching band at 1625 cm^{-1}, which shifts to 1595–1610 cm^{-1} in the coordination polymers indicating the involvement of the azomethine nitrogen in coordination (16). The two bands of medium intensity at ~1400 and ~1340 cm^{-1} are assigned to the vibration of the coordinated nitrate ion. The magnitudes of these bands indicate that the nitrate ion is coordinated in a bidentate fashion (17). The band observed in all the coordination polymers at 420 cm^{-1} may be assigned to the ν(M–N) mode (18). The band of medium intensity observed at 410–400 cm^{-1} is assigned to the ν(M–O) mode (19). The Schiff base shows a weak band at 2600 cm $^{-1}$, which is assigned to hydrogen-bonded O-H stretching

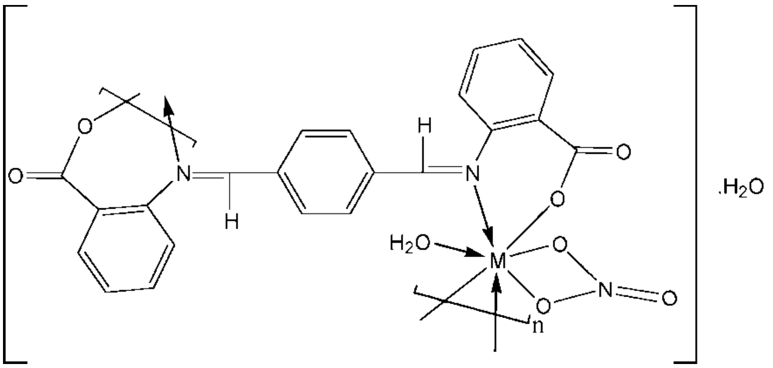

Figure 2. Suggested structure of the coordination chain polymer $[M(SB)(H_2O)(NO_3)]_n \cdot H_2O$

Downloaded At: 10:47 24 January 2011

Table 2
Infrared spectral data (cm^{-1}) of coordination polymers

Compound	υ(C═N)	υ(C═O)	υ(C—OH)	υ(COOH)	υ(COO) Asym.	υ(COO) Symm.	υ(M═O)	υ(M═N)
H_2SB	1625	1580	1350	2600	—	—	—	—
$[La(SB)(H_2O)(NO_3)]_n \cdot H_2O$	1590	—	—	—	1530	1370	410	400
$[Ce(SB)(H_2O)(NO_3)]_n \cdot H_2O$	1600	—	—	—	1540	1370	420	410
$[Pr(SB)(H_2O)(NO_3)]_n \cdot H_2O$	1590	—	—	—	1540	1380	420	410
$[Nd(SB)(H_2O)(NO_3)]_n \cdot H_2O$	1610	—	—	—	1540	1370	410	400
$[Sm(SB)(H_2O)(NO_3)]_n \cdot H_2O$	1600	—	—	—	1530	1380	410	400

H_2SB = N,N′-di(*o*-carboxyphenyl)terephthalaldehydediimine.

Downloaded At: 10:47 24 January 2011

Table 3

Electronic spectral data (cm^{-1}) and related bonding parameters of coordination polymers

Compound	$Ln(NO_3)_3$ electronic spectral bands	Compound electronic spectral bands	Energy levels	β	1-β	$b^{1/2}$	δ%	η
$[Pr(SB)(H_2O)(NO_3)]_n \cdot H_2O$	22470	22370	$^3H_4 \rightarrow {}^3P_2$	0.9955	0.0044	0.0331	0.4419	0.0023
	21280	21165	$\rightarrow {}^3P_1$	0.9945	0.0054	0.0367	0.5429	0.0027
	20830	20620	$\rightarrow {}^3P_0$	0.9899	0.0101	0.0502	1.0203	0.0025
	16950	16700	$\rightarrow {}^1D_2$	0.9852	0.0147	0.0606	1.4920	0.0075
$[Nd(SB)(H_2O)(NO_3)]_n \cdot H_2O$	19420	19250	$^4I_{9/2} \rightarrow {}^2G_{9/2}$	0.9913	0.0087	0.0467	0.8827	0.0044
	18993	18950	$\rightarrow {}^4G_{7/2}$	0.9977	0.0023	0.0239	0.2305	0.0012
	17390	17200	$\rightarrow {}^4G_{5/2}$	0.9891	0.0109	0.0522	1.1040	0.0055
	13420	13358	$\rightarrow {}^2S_{3/2}$	0.9953	0.0040	0.0339	0.4621	0.0024
	12500	12310	$\rightarrow {}^4F_{5/2}$	0.9848	0.0152	0.0616	1.5434	0.0076
	11446	11428	$\rightarrow {}^4F_{3/2}$	0.9984	0.0016	0.0200	0.1602	0.0008
$[Sm(SB)(H_2O)(NO_3)]_n \cdot H_2O$	24850	24691	$^6H_{5/2} \rightarrow {}^4F_{9/2}$	0.9936	0.0063	0.0396	0.6340	0.0032
	24100	24050	$\rightarrow {}^6P_{5/2}$	0.9979	0.0020	0.0223	0.2004	0.0011
	21600	21505	$\rightarrow {}^4I_{13/2}$	0.9956	0.0043	0.0327	0.4319	0.0022

H_2SB = N,N′-di(*o*-carboxyphenyl)terephthalaldehydediimine.

of carboxylic group. This band vanishes in the spectra of the coordination polymers indicating the involvement of carboxylic group ν(COOH) in chelation. The strong bands at 1580 and 1350 cm^{-1} in the Schiff base due to ν(C=O) and ν(C–OH) stretching disappear on chelation and these bands are replaced by two equivalent ν(C–O) bands. Intermediate in force constant between ν(C=O) and ν(C–OH) (20). Asymmetric and symmetric ν(COO) stretching bands appear at about 1540 and 1380 cm^{-1} in the coordination polymers. The data are summarized in Table 2.

Electronic Spectra

The electronic spectra of the nitrates of lanthanide are compared with the corresponding coordination polymers. La(III) and Ce(III) coordination polymers have no significant absorption in a visible region. The absorption bands appear in the spectra of the coordination polymers of Pr(III), Nd(III) and Sm(III) are due to transitions from the ground levels $^3H_4$, $^4I_{9/2}$ and $^6H_{5/2}$ to the excited J-levels of 4f configuration, respectively. Some red shift or nephelauxetic effect is observed in these coordination polymers. The data are summarized in Table 3. In all the coordination polymers, marked enhancement in the intensity of the bands has been observed. The red shift of the hypersensitive bands has been utilized to calculate the nephelauxetic effect (β) in these coordination polymers. From the β-values, the covalence factor ($b^{1/2}$), Sinha parameter ($\delta\%$) (metal-ligand covalency %) and the covalency angular overlap parameter (η), have been calculated using the expression (21), $b^{1/2} = 1/2(1-\beta)^{1/2}$, $\delta\% = [1-\beta/B] \times 100$, $\eta = (1-\beta^{1/2})/\beta^{1/2}$. The positive values for $(1-\beta)$ and $\delta\%$ in these coordination polymers suggest that the bonding between the metal and the ligand is covalent compared with the bonding between the metal and an aquo ion. The values of parameter (η) were found to be positive indicating covalent bonding. Based on the electronic spectral studies, a coordination number of seven around the metal ion (1).

Downloaded At: 10:47 24 January 2011

Thermogravimetric Analysis

It has been observed that all the coordination polymers show a loss in weight corresponding to one water molecule in the range 150 to 180°C, indicating that this water molecule, is coordinated to the metal ion (22). In between 35–105°C, the loss in weight for all coordination polymers corresponds to one water molecule. Because of the low temperatures this water of crystallization (23). The TG curves indicate that in the temperature range 350–400°C, the compounds start to lose nitrate ion. In the temperature range 400 to 800°C, the Schiff base molecules are lost. In all of the cases, the final products are metal oxides. These results are in good accordance with the composition of the coordination polymers.

Acknowledgement

The authors are thankful to Prof. R. M. Patel, Head, Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar, India, for providing the necessary laboratory facilities.

References

1. Gudasi, K.B. and Goudar, T.R. (2000) *Synth. React. Inorg. Met.-Org. Chem.*, 30 (10): 1859–1869.

2. Ajithkumar, G. and Radhakrishnan, P.K. (2002) *Synth. React. Inorg. Met.-Org. Chem.*, 32 (4): 831–842.
3. Siddiqi, K.S. and Khan, A.L. (1989) *Synth. React. Inorg. Met.-Org. Chem.*, 19: 41.
4. Braga, D. (2000) *Acc. Chem. Res.*, 33: 601; Robson, R., Abrahams, B.F., Batten, S.R., Gable, R.W., Hoskins, D.F., and Liu, J. (1992) *Supramolecular Architectures*, 256.
5. Hemmila, I.A., (Ed.). (1995) *Application of Fluorescence in Immunoassays*; Wiley: New York. Lakowicz, J.R. (1994) *Topics in Fluorescence Spectroscopy*; Plenum Press: New York, Vol. 4.
6. Prodi, L., Bolletta, F., Montalti, M., and Zaccheroni, N. (2000) *Coord. Chem. Rev.*, 205: 59–83; Fabbrizzi, L. Poggi, A. (1995) *Chem. Soc. Rev.* 197–202.
7. Matsui, H., Hasegawa, H., and Yoshihara, M. (2005) *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry*, 42: 869–876.
8. Patel, N.B., Patel, G.P., and Joshi, J.D. (2005) *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry*, 42: 931–943.
9. Xu, H., Liang, J., Zhuang, J., Kou, H., Wang, R., and Li, Y. (2004) *Journal of Molecular Structure*, 689: 177–181.
10. Cao, R., Sun, D., Liang, Y., Hong, M., Tatsumi, K., and Shi, Q. (2002) *Inorg. Chem.*, 41: 2087.
11. Patel, N.H., Panchal, P.K., and Patel, M.N. (2005) *Synth. React. Inorg. Met.-Org. and Nano-Met. Chem.*, 35: 107–110.
12. Patel, N.H., Patel, K.N., and Patel, M.N. (2002) *Synth. React. Inorg. Met.-Org. Chem.*, 32: 1879–1987.
13. Vogel, A.I. (1969) *A Textbook of Quantitative Inorganic Analysis*; 3rd ed.; ELBS Longman: London.
14. Bi, C., Fan, Y., Syn, G., Zheny, G., and Zhang, G. (2001) *Synth. React. Inorg. Met.-Org. Chem.*, 31 (2): 219–225.
15. Icbudak, H., Yilmaz, V.T., and Olemez, H.J. (1998) *Therm. Anal.*, 53: 843–854.
16. Madhu, N.T. and Radhakrishnan, P.K. (2000) *Transition Met. Chem.*, 25: 287–292.
17. Nakamoto, K. (1986) Coordination Compounds. In *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; John Wiley and Sons, Inc: New York, 254–257.
18. Dhammani, A., Bohra, R., and Mehrota, R.C. (1998) *Polyhedron.*, 17: 163–171.
19. Silverstein, R.M., Bassler, G.C., and Morril, T.C. (1991) Infrared Spectroscoppy. In *Spectrometric Identification of Organic Compounds*, 5th ed.; John Wiley and Sons, Inc: New York, 93.
20. Ali-Mohamed, A.Y. and Al-Arrayed, S.A.W. (2002) *Synth. React. Inorg. Met.-Org. Chem.*, 32 (10): 1759–1767.
21. Rao, T.R. and Kumar, P.A. (1995) *Synth. React. Inorg. Met.-Org. Chem.*, 25 (6): 1011–1026.
22. (1980) *Proceedings of the Sixth International Conference on Thermal Analysis*, Bayreuth, Germany.
23. Lunyu, Qu, Yingji, Sun, Yaguang, Chen, Ming, Yu, and Jun Peng (1994) *Synth. React. Inorg. Met.-Org. Chem.*, 24 (8): 1339.

Downloaded At: 10:47 24 January 2011