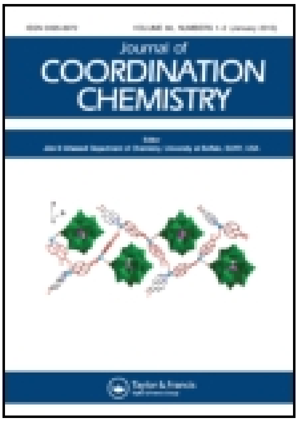
This article was downloaded by: [Renmin University of China]
On: 13 October 2013, At: 10:48
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Structures and thermal properties of strontium and barium 1,3-propanediaminetetraacetates

Mao-Long Chen [a] , Yu-Hui Hou [a] , Wen-Sheng Xia [a] & Zhao-Hui Zhou [a]
[a] State Key Laboratory of Physical Chemistry of Solid Surfaces, National Engineering Laboratory for Green Chemical Productions of Alcohols, Ethers and Esters , College of Chemistry and Chemical Engineering, Xiamen University , Xiamen , China

Accepted author version posted online: 25 Mar 2013.Published online: 09 May 2013.

To cite this article: Mao-Long Chen , Yu-Hui Hou , Wen-Sheng Xia & Zhao-Hui Zhou (2013) Structures and thermal properties of strontium and barium 1,3-propanediaminetetraacetates, Journal of Coordination Chemistry, 66:11, 1906-1915, DOI: 10.1080/00958972.2013.788693

To link to this article: http://dx.doi.org/10.1080/00958972.2013.788693

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

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

Journal of Coordination Chemistry, 2013
Vol. 66, No. 11, 1906–1915, http://dx.doi.org/10.1080/00958972.2013.788693

Structures and thermal properties of strontium and barium 1,3-propanediaminetetraacetates

MAO-LONG CHEN, YU-HUI HOU, WEN-SHENG XIA and ZHAO-HUI ZHOU*

State Key Laboratory of Physical Chemistry of Solid Surfaces, National Engineering Laboratory for Green Chemical Productions of Alcohols, Ethers and Esters, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, China

(*Received 12 November 2012; in final form 25 January 2013*)

In neutral and acidic solution, homonuclear s-block metal complexes $[Sr_2(1,3\text{-pdta})(H_2O)_{3.5}]_n$ (**1**), $\{[Ba_2(1,3\text{-pdta})(H_2O)_6]\cdot H_2O\}_n$ (**2**), $\{[Sr(1,3\text{-}H_2pdta)]\cdot(H_2O)\}_n$ (**3**), and $[Ba(1,3\text{-}H_2pdta)(H_2O)_3]_n$ (**4**) {1,3-H_4pdta=1,3-propanediamine-*N*,*N*,*N′*,*N′*-tetraacetic acid, $CH_2[CH_2N(CH_2CO_2H)_2]_2$} were isolated. In **1** and **2**, hexadentate 1,3-pdta joins two metal ions via the diamine chain. In **3** and **4**, the nitrogens of 1,3-H_2pdta were protonated and show no coordination. There is no coordinated water in **3**, unusual coordination for strontium. In **4**, the coordination number is nine and there are three coordinated waters for each barium. One carboxy group of pdta is free without coordination. Thermal decomposition shows that temperatures of ligand elimination start at 408, 423, 298, and 250 °C for **1**–**4**, respectively. Acidic condition is favorable for preparation of metal oxide at low temperature.

Keywords: 1,3-Propanediaminetetraacetic acid; Barium; Strontium; Thermal decomposition; Coordination mode

1. Introduction

The deprotonated tetraanion of 1,3-propanediaminetetraacetic acid forms water-soluble monomeric chelates with a plethora of polyvalent metal ions. It coordinates through four carboxy oxygens and two nitrogens, that is, $[M'^{II}(H_2O)_6][M^{II}(1,3\text{-pdta})]\cdot 2H_2O$ (M = Mg [1], Ca [1], Co [2, 3], Ni [4, 5], Cu [4, 6, 7], and Zn [8]), $[M'^{II}(H_2O)_6][M^{II}(1,3\text{-pdta})(H_2O)]\cdot 2H_2O$ (M = Mn [9] and Cd [8, 9]), and $M'[M^{III}(1,3\text{-pdta})]\cdot xH_2O$ (M = Fe [10], Ru [11], V [12], Cr and Rh [13]). The structural preferences of metal complexes with hexadentate 1,3-pdta, which has one more methylene with respect to edta [H_4edta = ethylenediaminetetraacetic acid, $(HO_2CH_2C)_2NCH_2CH_2N(CH_2CO_2H)_2$] in the diamine chain, have been considered in terms of the central metal ion size, d-electron configuration, and the counter cation [12–16], where edta is a much more common aminopolycarboxylate. Some pdta complexes of main group elements [1, 17–19] and rare earth elements [20–29] were also studied. Interest in alkaline earth carboxylates expands because of their potential use as precursors of materials in superconductors [30–36] and catalysts like oxidative coupling of methane [37–48] and their structural diversity when forming metal organic frameworks or coordination polymers [49–57]. Herein, we report structural and spectral characterizations and thermal

---

*Corresponding author. Email: zhzhou@xmu.edu.cn properties of alkaline earth metal complexes $[Sr_2(1,3\text{-pdta})(H_2O)_{3.5}]_n$ (**1**), $\{[Ba_2(1,3\text{-pdta})(H_2O)_6]\cdot H_2O\}_n$ (**2**), $\{[Sr(1,3\text{-}H_2pdta)]\cdot(H_2O)\}_n$ (**3**), and $[Ba(1,3\text{-}H_2pdta)(H_2O)_3]_n$ (**4**) isolated in neutral and acidic solutions, respectively, where nitrogens of pdta are protonated and show no coordination in **3** and **4**.

2. Experimental

2.1. *Physical measurements*

The chemicals used were analytical grade reagents. The pH was measured by potentiometric method with a digital PHB-8 pH meter. Infrared spectra were recorded as Nujol mulls between KBr plates on a Nicolet 330 FT-IR spectrometer. Elemental analyses were performed with an EA 1110 elemental analyzer. Thermogravimetric analyses were recorded on TG 209F1 thermal analyzers, under an air flow of 20 mL/min at a heating rate of 10 °C min^{-1}. Powder X-ray diffraction data were collected using monochromated Cu Kα radiation on a Phillips X'Pert diffractometer.

2.2. *Preparations of $[Sr_2(1,3\text{-pdta})(H_2O)_{3.5}]_n$ (1) and $\{[Ba_2(1,3\text{-pdta})(H_2O)_6]\cdot H_2O\}_n$ (2)*

1,3-Propanediaminetetraacetic acid (0.60 g, 2.0 mM) was added to a stirred solution of strontium nitrate (0.85 g, 4.0 mM) in water (15 mL). The pH of the solution was adjusted to 6.0 by dilute ammonium hydroxide (5.0 M L^{-1}, ~1.6 mL). The mixture was stirred for 2 h at room temperature. The solution was left to evaporate for several days and gave colorless crystalline **1**, isolated by filtration, washed with ethanol, and dried in air. Yield: 0.72 g (67%). IR (KBr, cm^{-1}): 3427_{vs}, 3250_{s}, 2955_{m}, 2891_{m}, 2835_{s}, 2757_{w}, 1589_{vs}, 1409_{vs}, 1333_{s}, 1299_{m}, 1239_{m}, 1146_{m}, 1121_{m}, 1058_{w}, 983_{w}, 936_{w}, 913_{w}, 887_{w}, 772_{w}, 738_{m}, 715_{m}, 644_{m}, 568_{m}, 537_{m}, 474_{w}; Anal. Calcd for $C_{11}H_{21}N_2O_{11.5}Sr_2$: C, 24.4; H, 3.9; N, 5.2. Found: C, 24.5; H, 4.1; N, 5.2 (%). Similarly, barium chloride (0.83 g, 4.0 mM) was used as a starting material for the preparation of barium pdta complex. Colorless crystalline **2** was isolated with a yield of 1.1 g (79%). IR (KBr, cm^{-1}): $3442_{m,br}$, 3947_{w}, 2904_{m}, 2869_{m}, 2819_{m}, 2741_{w}, 1597_{vs}, 1569_{vs}, 1436_{vs}, 1407_{vs}, 1330_{s}, 1262_{s}, 1162_{w}, 1126_{s}, 1070_{w}, 9999_{m}, 980_{m}, 930_{m}, 884_{w}, 858_{w}, 727_{m}, 631_{m}, 549_{w}, 520_{w}; Anal. Calcd for $C_{11}H_{28}N_2O_{15}Ba_2$: C, 18.8; H, 4.0; N, 4.0. Found: C, 19.0; H, 3.9; N, 3.8 (%).

2.3. *Preparations of $\{[Sr(1,3\text{-}H_2pdta)]\cdot(H_2O)\}_n$ (3) and $[Ba(1,3\text{-}H_2pdta)(H_2O)_3]_n$ (4)*

1,3-Propanediaminetetraacedic acid (0.60 g, 2.0 mM) was added to a stirred solution of strontium nitrate (0.42 g, 2.0 mM) in water (15 mL). The pH of the solution was adjusted to 2.5 by dilute ammonium hydroxide (2.0 M L^{-1}, ~2.0 mL). The mixture was stirred for 2 h at room temperature and left to evaporate for several days giving colorless crystalline product. **3** was isolated by filtration, washed with ethanol, and dried in air. Yield: 0.63 g (77%). IR (KBr, cm^{-1}): 3429_{s}, 3050_{m}, 3008_{m}, 2953_{m}, 1630_{vs}, 1433_{s}, 1387_{vs}, 1360_{s}, 1310_{s}, 1240_{w}, 1198_{w}, 1114_{m}, 1057_{w}, 993_{w}, 952_{w}, 897_{m}, 695_{m}, 606_{w}, 564_{w}, 498_{m}, 405_{w}; Anal. Calcd for $C_{11}H_{18}N_2O_9Sr$: C, 32.2; H, 4.4; N, 6.8. Found: C, 32.0; H, 4.3; N, 6.8 (%). Similarly, barium chloride (0.41 g, 2.0 mM) was used as a starting material at pH 2.5 giving colorless crystalline **4** with a yield of 0.80 g (81%). IR (KBr, cm^{-1}): 3431_{vs}, 3034_{s}, 2824_{w}, 1672_{s}, 1626_{vs}, 1435_{s}, 1407_{vs}, 1368_{vs}, 1335_{vs}, 1320_{s}, 1305_{m}, 1287_{m}, 1225_{m}, 1201_{w},

1105_w, 1077_w, 1052_m, 979_m, 953_w, 925_m, 900_m, 877_w, 772_w, 697_m, 617_m, 565_m, 535_m, 470_w, 404_w; Anal. Calcd for $C_{11}H_{22}BaN_2O_{11}$: C, 26.7; H, 4.5; N, 5.7. Found: C, 26.5; H, 4.3; N, 5.5 (%).

2.4. *X-ray data collections, structure solutions, and refinements*

Suitable single crystals of **1–4** were selected and mounted onto thin glass fibers quickly. X-ray intensity data for **1–4** were measured at 173 K on an Oxford CCD diffractometer with Mo Kα radiation ($\lambda = 0.71073$ Å). Empirical adsorption correction was applied to all data using SADABS and CrysAlis (multi-scan) program. The initial models were obtained through direct methods, and completion of the structures was achieved by difference Fourier strategies. The structures were refined by least squares on F^2, with anisotropic displacement parameters for non-H atoms. All calculations to solve and refine the structures and to obtain derived results were carried out with SHELXS 97 and SHELXL 97. Full use of the CCDC package was also made for searching in the CSD database [58, 59]. Crystal data and structural refinements for **1–4** are summarized in table 1.

3. Results and discussion

3.1. *Synthesis*

The pH controls for syntheses of **1** and **2** were in neutral water solution. The synthetic conditions were similar except for different metal ions. The molar ratio of M : pdta is 2 : 1.

Table 1. Crystallographic data and structural refinements for $[Sr_2(1,3\text{-pdta})(H_2O)_{3.5}]_n$ (**1**), $\{[Ba_2(1,3\text{-pdta})(H_2O)_6]\cdot H_2O\}_n$ (**2**), $\{[Sr(1,3\text{-}H_2pdta)]\cdot(H_2O)\}_n$ (**3**) and $[Ba(1,3\text{-}H_2pdta)(H_2O)_3]_n$ (**4**).

Compound references	**1**	**2**	**3**	**4**
Chemical formula	$C_{11}H_{21}N_2O_{11\cdot 50}Sr_2$	$C_{11}H_{28}N_2O_{15}Ba_2$	$C_{11}H_{18}N_2O_9Sr$	$C_{11}H_{22}N_2O_{11}Ba$
Formula mass	540.54	703.03	409.89	495.65
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Triclinic
a/Å	21.8084(8)	11.8903(2)	14.9064(5)	7.5599(2)
b/Å	9.4658(3)	13.4983(3)	12.0623(4)	9.0786(3)
c/Å	8.6521(3)	13.7306(3)	8.1118(3)	13.5165(5)
α/°				101.255(3)
β/°	95.786(3)		108.706(4)	101.948(3)
γ/°				107.605(3)
Unit cell volume/Å^3	1777.0(1)	2203.75(8)	1381.50(8)	831.36(5)
Temperature/K	173(2)			
Space group	$P2_1/c$	$P2_12_12_1$	$C2/c$	$P\bar{1}$
No. of units per unit cell, Z	4	4	4	2
Radiation type	Mo Kα	Mo Kα	Mo Kα	Mo Kα
Absorption coefficient, μ/mm^{-1}	6.067	3.625	3.958	2.451
No. of reflections measured	14,809	16,486	5523	14,496
No. of independent reflections	3674	5066	1589	3815
R_{int}	0.0676	0.0524	0.0552	0.0453
Final R_1 values $[I > 2\sigma(I)]$	0.0564	0.0316	0.0365	0.0211
Final wR(F^2) values $[I > 2\sigma(I)]$	0.0928	0.0503	0.0740	0.0434
Final R_1 values (all data)	0.0717	0.0361	0.0506	0.0230
Final wR(F^2) values (all data)	0.0970	0.0517	0.0793	0.0440
Goodness of fit on F^2	1.220	1.029	1.098	1.091
Max. and min. Δρ (e Å^3)	0.970 and −0.842	0.671 and −0.567	0.562 and −0.545	0.520 and −0.894

Syntheses of **3** and **4** were carried out in acidic aqueous solutions. The molar ratio of M : pdta is 1 : 1. Complexes $[Sr_2(1,3\text{-pdta})(H_2O)_{3.5}]_n$ (**1**), $\{[Ba_2(1,3\text{-pdta})(H_2O)_6]\cdot H_2O\}_n$ (**2**), $\{[Sr(1,3\text{-}H_2pdta)]\cdot(H_2O)\}_n$ (**3**), and $[Ba(1,3\text{-}H_2pdta)(H_2O)_3]_n$ (**4**) can be isolated in high yields as coordination polymers, which are insoluble in water.

3.2. *Structural descriptions of 1–4*

Figures 1–4 show perspective views of **1–4** at 30% probability levels. Packing diagrams of **1–4** are shown in Supplementary material. In the crystal structures of **1** and **2**, 1,3-pdta coordinates in bis-tridentate mode. Barium salt **2** is isomorphous with $\{[Sr_2(1,3\text{-pdta})(H_2O)_6]\cdot H_2O\}_n$ [18]. The coordination numbers of Sr and Ba are nine in **1** and **2**. In **1**, there are two different coordination modes of Sr. One is surrounded by a nitrogen, six carboxy oxygens, and two waters, the other is surrounded by a nitrogen, four carboxy oxygens, and four waters. Occupancy of O3w [Sr1−O3w, 2.807(8) Å, Sr1′−O3w, −*x*, −*y*, 1−*z*, 4.142(8) Å] with the remarkably short distance of 1.907(8) Å between O3w and O3w′ (−*x*, −*y*, 1−*z*) was determined to be 50%. Thus, each water was found on one side of Sr1. This is similar to that of O1w which bridged two Sr2 ions [3.245(6) and 2.748(5) Å]. In **2**, there is only one coordination mode of Ba, surrounded by one nitrogen, four carboxy oxygens, and four waters. There are seven waters in an asymmetric unit, where six waters coordinate with barium. Of the six coordinated waters, two (O1w and O4w) bridge as shown in Supplementary material. Each Ba ion is triply bridged to two Ba ions. The triple bridging mode is achieved via one water and two oxygens, each attached to different carboxy groups. In a previous report [18], barium pdta 2 : 1 complex was considered as a new type of structure based on IR and powder diffraction. Our structural analysis shows it shares a similar bis-tridentate coordination as strontium pdta complex, where IR spectra are similar [18].

In **3** and **4**, nitrogen of the amine is protonated and shows no coordination with Sr and Ba. In **3**, there is no coordinated water. The coordination number of Sr is eight with H_2pdta octadentate. Each pdta uses its two carboxy groups attached to different nitrogens to form a 12 member chelate ring. The two carboxy groups also bridge two other Sr ions; pdta uses two oxygens from the other two carboxy groups to coordinate with four Sr ions, one bridging with two Sr ions. In **4**, the coordination number of Ba is nine. Each pdta uses two carboxy groups attached to one nitrogen to form an eight member chelate ring. The two carboxy groups also bridge two other Ba ions forming a 1-D chain, while one carboxy is not coordinated but forms hydrogen bonds [O5···O3w 2.737(2) Å; O6···O1wa 2.810(2) Å; O6···O2wb 2.758(2) Å; a, *x*−1, *y*, *z*−1; b, *x*−2, *y*, *z*−1] between two chains to form a 3-D supramolecule as shown in Supplementary material.

Comparisons of bond distances (Å) between coordinated carboxy, water, and amine are shown in table 2. Selective bond distances for **1–4** are shown in table S1. As shown in table 2, all pdta ligands are hexadentate when coordinated with transition metal ions in neutral solution [2–16]. In s-block metals Ca, Sr, and Ba, the dentate number is larger than 10. For strontium, the coordination number is nine, but the dentate numbers are different. In acidic solution, pdta is hexadentate, tetradentate, or bidentate in zinc complexes [60, 61]. In s-block metals, the dentate number is eight and six for Sr and Ba, respectively. It is concluded that the dentate numbers decrease with decreases of solution pH. From table 2, we still can find out that **1** and **3** have the shortest bond distances in all strontium and barium complexes and show less coordinated water in asymmetric units.

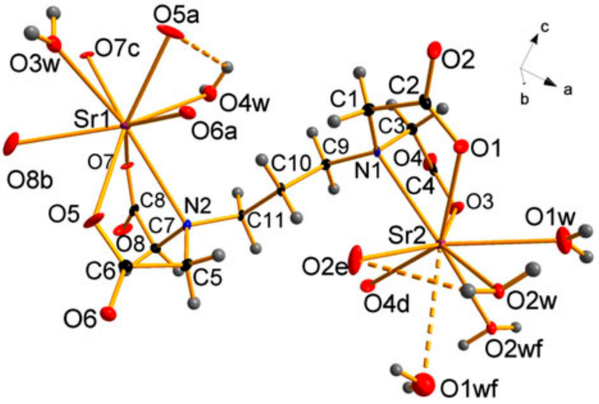


Figure 1. Perspective view of $[Sr_2(1,3\text{-pdta})(H_2O)_{3.5}]_n$ (**1**) at 30% probability levels. Symmetry codes: *a*, *x*, –*y* + ½, *z* + ½; *b*, –*x*, *y* – ½, –*z* + ½; *c*, –*x*, –*y* + 1, –*z* + 1; *d*, *x*, –*y* + 3/2, *z* – ½; *e*, *x*, –*y* + ½, *z* – ½; *f*, –*x* + 1, –*y* + 1, –*z* + 1.

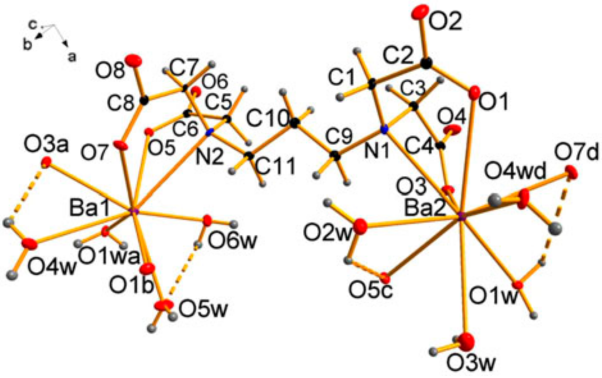


Figure 2. Perspective view of $\{[Ba_2(1,3\text{-pdta})(H_2O)_6]\cdot H_2O\}_n$ (**2**) at 30% probability levels. Symmetry codes: *a*, *x* – ½, –*y* – ½, –*z* + 1; *b*, –*x*, *y* + ½, –*z* + ½; *c*, *x* + ½, –*y* – ½, –*z* + 1; *d*, –*x*, *y* – ½, –*z* + ½.

The coordination numbers of eight and nine show no difference for different pH values for strontium and barium pdta complexes, but are related to the nature of metal ions. Denticity of pdta shows a relationship with pH.

3.3. *Coordination modes of pdta ligand*

The coordination modes of pdta ligand are listed in scheme 1. Type *a* is the most common mode in transition and Mg and Ca metals [1–13]. In this type, pdta uses its two nitrogens and four oxygens from carboxy groups to chelate one center ion. Type *b* can be found in molybdenum [14] and Sr and Ba complexes like **1**, **2** and $\{[Sr_2(1,3\text{-pdta})(H_2O)_6]\cdot H_2O\}_n$ [18]; pdta ligands lose chelating properties of the diamine and form bis-tridentate complexes. Type *c* can be found in **3**, where nitrogens of pdta are protonated without coordination; pdta uses its two oxygens to chelate with one Sr ion and form a 12 member chelate ring. Type *d* can be found in **4**. Nitrogens of the ligand are also protonated and do

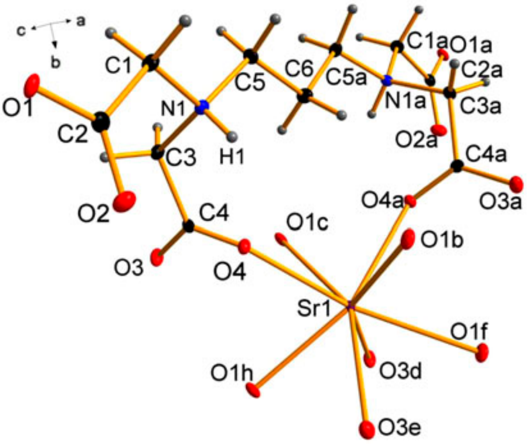


Figure 3. Perspective view of $\{[Sr(1,3\text{-}H_2pdta)]\cdot(H_2O)\}_n$ (**3**) at 30% probability levels. Symmetry codes: *a*, *–x + 1, y, –z + ½*; *b*, *–x + ½, y + ½, –z + ½*; *c*, *x + ½, y + ½, z*; *d*, *–x + 1, –y + 1, –z + 1*; *e*, *x, –y + 1, z – ½*; *f*, *–x + ½, –y + ½, –z*; *h*, *x + ½,–y + ½, z + ½*.

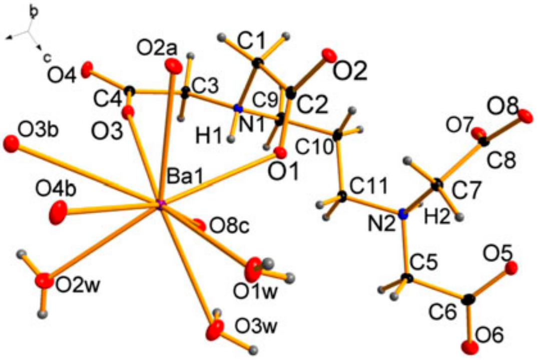


Figure 4. Perspective view of $[Ba(1,3\text{-}H_2pdta)(H_2O)_3]_n$ (**4**) at 30% probability levels. Symmetry codes: *a*, *–x + 1,–y,–z*; *b, –x + 2, –y,–z*; *c, x + 1, y, z*.

not coordinate with Ba ions, but its two carboxy groups chelate with one Ba forming an eight member chelate ring.

3.4. *IR spectroscopy*

The IR spectra of **1–4** (Supplementary material) show characteristic bands of carboxy groups. Strong peaks at 1589, 1409, 1333 cm^{-1} for **1**, 1597, 1569, 1436, 1407, 1330 cm^{-1} for **2**, 1630, 1433, 1387, 1360, 1310 cm^{-1} for **3**, 1672, 1626, 1435, 1407, 1368, 1335, and 1320 cm^{-1} for **4** correspond to v_{as} and v_s vibrations of the coordinated carboxy groups [62]. The $v_{as}(CO_2)$ of **1** is at 1589 cm^{-1} and red-shifts 41 cm^{-1} compared with that of **3** (1630 cm^{-1}), $v_s(CO_2)$ of **1** is at 1409 cm^{-1} and blue-shifts 21 cm^{-1} compared with that of **3** (1387 cm^{-1}). These changes confirm that oxygens from carboxy groups of $[pdta]^{4-}$ in **1**

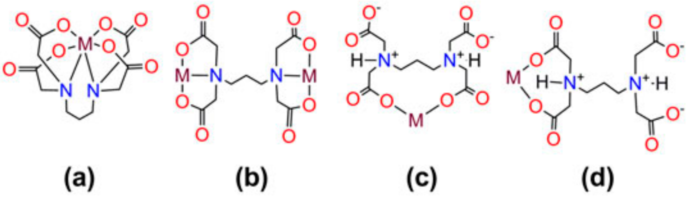
Table 2. Comparisons of bond distances (Å) between coordinated carboxy, water and amine groups, coordination numbers and denticity in pdta complexes.

Compounds	M–O$_{carboxy}$	M–O$_w$	M–N	CN	Denticity	Refs
Neutral solution						
$Mg(H_2O)_6][Mg(1,3\text{-pdta})]\cdot 2H_2O$	2.051(2)	–	2.199(2)	6	6	[1]
$[Ca(H_2O)_3Ca(1,3\text{-pdta})(H_2O)]\cdot 2H_2O$	2.415(4)	2.553(4)	2.681(4)	8	11	[1]
$Mg(H_2O)_6][Co(1,3\text{-pdta})]\cdot 2H_2O$	2.083(2)	–	2.142(2)	6	6	[2]
$Mg(H_2O)_6][Ni(1,3\text{-pdta})]\cdot 2H_2O$	2.052(5)	–	2.073(5)	6	6	[5]
$Mg(H_2O)_6][Cu(1,3\text{-pdta})]\cdot 2H_2O$	2.123(2)	–	2.047(2)	6	6	[6]
$Mn(H_2O)_6][Cu(1,3\text{-pdta})]\cdot 2H_2O$	2.129(2)	–	2.049(2)	6	6	[7]
$Mg(H_2O)_6][Zn(1,3\text{-pdta})]\cdot 2H_2O$	2.092(3)	–	2.155(2)	6	6	[8]
$[Mg(H_2O)_6][Mn(1,3\text{-pdta})(H_2O)]\cdot 2H_2O$	2.314(3)	2.154(5)	2.429(4)	7	6	[9]
$[Mg(H_2O)_6][Cd(1,3\text{-pdta})(H_2O)]\cdot 2H_2O$	2.410(1)	2.252(2)	2.442(1)	7	6	[8]
$\{[Sr_2(1,3\text{-pdta})(H_2O)_6]\cdot H_2O\}_n$	2.78(1)	2.85(2)	2.98(1)	9	10	[8]
$[Sr_2(1,3\text{-pdta})(H_2O)_{3.5}]_n$ (**1**)	2.586(5)	2.776(8)	2.832(4)	9	12	This work
$\{[Ba_2(1,3\text{-pdta})(H_2O)_6]\cdot H_2O\}_n$ (**2**)	2.790(4)	2.851(5)	2.955(4)	9	10	This work
Acidic solution						
$K_{2n}[ZnCl_2(1,3\text{-}H_2pdta)ZnCl_2]_n$	1.975(3)	–	–	4	4	[60]
$[ZnI_2(H_2O)(1,3\text{-}H_4pdta)]_n$	2.236(6)	2.04(1)	–	5	2	[60]
$[Zn(NO_3)_2(H_2O)(1,3\text{-}H_4pdta)]_n$	2.075(2)	2.020(4)	–	5	2	[61]
$[ZnBr_2(H_2O)(1,3\text{-}H_4pdta)]_n$	2.304(6)	1.992(6)	–	5	2	[61]
$[Zn(NCS)_2(H_2O)(1,3\text{-}H_4pdta)]_n$	2.175(3)	1.986(4)	–	5	2	[61]
$\{[Sr(1,3\text{-}H_2pdta)]\cdot(H_2O)\}_n$ (**3**)	2.598(2)	–	–	8	8	This work
$[Ba(1,3\text{-}H_2pdta)(H_2O)_3]_n$ (**4**)	2.812(2)	2.793(2)	–	9	6	This work

coordinated stronger than in **3**. Similar results can be found in **2** and **4**. In **4**, there exists a band at 1672 cm^{-1}, attributed to the uncoordinated carboxy of pdta, consistent with structural analysis.

3.5. *Thermogravimetric analyses (TGA)*

Thermal stability and decomposition patterns of the complexes were investigated by thermogravimetric analyses. Supplementary material shows the TG curves of **1–4**. The TG-DTG curves are listed in Supplementary material. Data analyses are listed in table S2. The first big weight loss of **1** and **2** between 100 and 160 °C corresponds to loss of crystal waters. The next mass reductions occur at 408 and 423 °C for **1** and **2**, respectively, corresponding to ligand elimination from the complexes, assigned to weight loss of pdta. The weight is stable until 800 °C. The decomposition patterns of **1** and **2** are very similar. The residues are strontium oxide for **1** and barium oxide for **2**. For **3**, the first weight loss starts at 298 °C and follows at 383 and 439 °C. The decomposition pattern of **4** is similar to that of **3** except for a big weight loss at 119 °C for water molecules as shown in



Scheme 1. Coordination modes of pdta.

table S2. The residues are strontium oxide for **3** and barium oxide for **4**. Based on comparison of thermal patterns, acidic conditions may be favorable for preparation of metal oxide at low temperature.

4. Conclusions

1,3-Propanediaminetetraacetato s-block metal complexes have been isolated from reactions of $Sr(NO_3)_2/BaCl_2$ and pdta at neutral and acidic conditions. Spectral and structural analyses display that pdta ligands coordinate in three different modes. In $[Sr_2(1,3\text{-pdta})(H_2O)_{3.5}]_n$ (**1**) and $\{[Ba_2(1,3\text{-pdta})(H_2O)_6]\cdot H_2O\}_n$ (**2**), pdta is bis-tridentate. In $\{[Sr(1,3\text{-}H_2pdta)]\cdot(H_2O)\}_n$ (**3**) and $[Ba(1,3\text{-}H_2pdta)(H_2O)_3]_n$ (**4**), nitrogens of pdta are protonated and show no coordination; pdta uses two oxygens to chelate with one Sr and form a 12 member chelate ring in **3**, while it uses two carboxy groups from the same nitrogen to chelate with one Ba, forming an eight member chelate ring in **4**. Due to protonations of nitrogens in **3** and **4**, metal oxide is easily obtained at low temperature.

Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 887484–887487 for **1–4**. Copies of this information may be obtained free of charge from The Director, CCDC 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

Financial contributions from the National Science Foundation of China (21073150) and the National Basic Research Program of China (2010CB732303) are gratefully acknowledged.

References

[1] D.D. Radanović, U. Rychlewska, M.I. Djuran, B. Warżajtis, N.S. Draskovic, D.M. Guresic. *Polyhedron*, **23**, 2183 (2004).

[2] D.D. Radanović, U. Rychlewska, M.I. Djuran, N.S. Draskovic, M.M. Vasojevic, I.M. Hodzic, D.J. Radanović. *Polyhedron*, **22**, 2745 (2003).

[3] N.S. Draskovic, M.I. Djuran, M.S. Cvijovic, D.D. Radanović, V. Jevtovic. *Transition Met. Chem.*, **29**, 874 (2004).

[4] A. Mederos, P. Gili, S. Dominguez, A. Benitez, M.S. Palacios, M. Hernandezpadilla, P. Martinzarza, M.L. Rodriguez, C. Ruizperez, F.J. Lahoz, L.A. Oro, F. Brito, J.M. Arrieta, M. Vlassi, G. Germain. *J. Chem. Soc. Dalton Trans.*, 1477 (1990).

[5] D.J. Radanović, T. Ama, H. Kawaguchi, N.S. Draskovic, D.M. Ristanovic, S. Janicijevic. *Bull. Chem. Soc. Jpn.*, **74**, 701 (2001).

[6] U. Rychlewska, D.D. Radanović, V.S. Jevtovic, D.J. Radanović. *Polyhedron*, **19**, 1 (2000).

[7] M. Hernandez-Padilla, E. Chinea, S. Dominguez, A. Mederos, M.C. Munoz, F. Lloret. *Polyhedron*, **19**, 1175 (2000).

[8] U. Rychlewska, D.M. Gurešić, B. Warżajtis, D.D. Radanović, M.I. Djuran. *Polyhedron*, **24**, 2009 (2005).

[9] U. Rychlewska, B. Warżajtis, D. Cvetic, D.D. Radanović, D.M. Guresić, M.I. Djuran. *Polyhedron*, **26**, 1717 (2007).

[10] R. Meier, J. Maigut, B. Kallies, N. Lehnert, F. Paulat, F.W. Heinemann, G. Zahn, M.P. Feth, H. Krautscheid, R. van Eldik. *Chem. Commun.*, **3960**, (2007).

[11] M.M.T. Khan, H.C. Bajaj, Z. Shirin, K. Venkatasubramanian. *Polyhedron*, **11**, 1059 (1992).

[12] J.C. Robles, Y. Matsuzaka, S. Inomata, M. Shimoi, W. Mori, H. Ogino. *Inorg. Chem.*, **32**, 13 (1993).

[13] R. Herak, G. Srdanov, M.I. Djuran, D.J. Radanović, M. Bruvo. *Inorg. Chim. Acta*, **83**, 55 (1984).

[14] G.-G. Gao, L. Xu, X.-S. Qu, H. Liu, Y.-Y. Yang. *Inorg. Chem.*, **47**, 3402 (2008).

[15] S.B. Yu, M. Droege, S. Downey, B. Segal, W. Newcomb, T. Sanderson, S. Crofts, S. Suravajjala, E. Bacon, W. Earley, D. Delecki, A.D. Watson. *Inorg. Chem.*, **40**, 1576 (2001).

[16] K. Krot, A.L. Llamas-Saiz, N. Vembu, K.B. Nolan. *Z. Anorg. Allg. Chem.*, **633**, 1900 (2007).

[17] S.Z. Hu, L.D. Tu, Y.Q. Huang, Z.X. Li. *Inorg. Chim. Acta*, **232**, 161 (1995).

[18] U. Rychlewska, B. Warżajtis, D.D. Radanović, N.S. Drasković, I.M. Stanojević, M.I. Djuran. *Polyhedron*, **30**, 983 (2011).

[19] J. Wang, G.R. Gao, Z.H. Zhang, X.D. Zhang, X.Z. Liu, Y.M. Kong, Y. Li. *Russ. J. Coord. Chem.*, **33**, 258 (2007).

[20] B. Liu, J. Wang, X. Wang, B.-M. Liu, L.-L. He, S.-K. Xu. *Spectrochim. Acta, Part A*, **77**, 1115 (2010).

[21] J. Gao, D. Li, J. Wang, X. Jin, P. Kang, T. Wu, K. Li, X. Zhang. *J. Coord. Chem.*, **64**, 2284 (2011).

[22] B. Liu, P. Hu, J. Wang, R. Xu, L.Q. Zhang, J. Gao, Y.F. Wang, X.D. Zhang. *Russ. J. Coord. Chem.*, **35**, 758 (2009).

[23] J. Wang, P. Hu, B. Liu, X. Chen, L.Q. Zhang, G.X. Han, R. Xu, X.D. Zhang. *Russ. J. Inorg. Chem.*, **55**, 1567 (2010).

[24] J. Wang, G.R. Gao, Z.H. Zhang, X.D. Zhang, X.Z. Liu, Y.M. Kong, Y. Li. *J. Coord. Chem.*, **59**, 2113 (2006).

[25] X. Chen, D. Li, J. Wang, B. Liu, Y. Kong, D. Wang, X. Zhang. *J. Coord. Chem.*, **63**, 3897 (2010).

[26] J. Wang, D. Li, J. Gao, B. Liu, B. Wang, D. Wang, T. Fan, X. Zhang. *J. Coord. Chem.*, **63**, 3792 (2010).

[27] J. Wang, P. Hu, B. Liu, R. Xu, X. Wang, L. Xu, L.Q. Zhang, X.D. Zhang. *Russ. J. Coord. Chem.*, **36**, 66 (2010).

[28] J. Wang, P. Hu, B. Liu, R. Xu, X. Wang, D. Wang, L.Q. Zhang, X.D. Zhang. *J. Struct. Chem.*, **52**, 568 (2011).

[29] J. Wang, P. Hu, G. Han, L. Zhang, D. Li, R. Xu, X. Chen, X.D. Zhang. *J. Struct. Chem.*, **52**, 575 (2011).

[30] A.R. Jurelo, J. Flemming, F.C. Serbena, C.R. Carubelli, P. Rodrigues, Jr., C.E. Foerster, F.T. Dias, I.O. de Carvalho Masson, I. Mazarro. *J. Cryst. Growth*, **311**, 3539 (2009).

[31] I. Nagai, Y. Abe, M. Kato, Y. Koike, A. Kakihana. *Solid State Ionics*, **151**, 265 (2002).

[32] J.H. Schon, M. Dorget, F.C. Beuran, X.Z. Zu, E. Arushanov, C.D. Cavellin, M. Lagues. *Nature*, **414**, 434 (2001).

[33] M. Valldor, I. Bryntse, A. Morawski. *Physica C*, **314**, 27 (1999).

[34] M.G. Francesconi, P.R. Slater, J.P. Hodges, C. Greaves, P.P. Edwards, M. Al–Mamouri, M. Slaski. *J. Solid State Chem.*, **135**, 17 (1998).

[35] T. Hashimoto, K. Kitazawa, M. Nakabayashi, T. Shiraishi, Y. Suemune, T. Yamamoto, H. Koinuma. *Appl. Organomet. Chem.*, **5**, 325 (1991).

[36] L.R. Morss, D.C. Sonnenberger, R.J. Thorn. *Inorg. Chem.*, **27**, 2106 (1988).

[37] H.Y. Wang, E. Ruckenstein. *J. Catal.*, **199**, 309 (2001).

[38] H.L. Wan, X.P. Zhou, W.Z. Weng, R.Q. Long, Z.S. Chao, W.D. Zhang, M.S. Chen, J.Z. Luo, S.Q. Zhou. *Catal. Today*, **51**, 161 (1999).

[39] V.R. Choudhary, A.M. Rajput, A.S. Mamman. *J. Catal.*, **178**, 576 (1998).

[40] V.R. Choudhary, B.S. Uphade, A.S. Mamman. *J. Catal.*, **172**, 281 (1997).

[41] E. Ruckenstein, Y.H. Hu. *Appl. Catal., A*, **133**, 149 (1995).

[42] T. Ohno, J.B. Moffat. *Catal. Lett.*, **9**, 23 (1991).

[43] Y. Amenomiya, V.I. Birss, M. Goledzinowski, J. Galuszka, A.R. Sanger. *Cat. Rev. Sci. Eng.*, **32**, 163 (1990).

[44] S. Ahmed, J.B. Moffat. *J. Catal.*, **121**, 408 (1990).

[45] S. Ahmed, J.B. Moffat. *Appl. Catal.*, **58**, 83 (1990).

[46] H. Nagamoto, K. Amanuma, H. Nobutomo, H. Inoue. *Chem. Lett.*, 237 (1988).

[47] J.M. Deboy, R.F. Hicks. *Ind. Eng. Chem. Res.*, **27**, 1577 (1988).

[48] K. Fujimoto, S. Hashimoto, K. Asami, H. Tominaga. *Chem. Lett.*, 2157 (1987).

[49] B.H. Hamilton, K.A. Kelly, W. Malasi, C.J. Ziegler. *Inorg. Chem.*, **42**, 3067 (2003).

[50] E.H. Falcao, Naraso, R.K. Feller, G. Wu, F. Wudl, A.K. Cheetham. *Inorg. Chem.*, **47**, 8336 (2008).

[51] S. Natarajan, J.K. Sundar, S. Athimoolam, B.R. Srinivasan. *J. Coord. Chem.*, **64**, 2274 (2011).

[52] P.J. Rosado, K. Ruhlandt-Senge. *J. Coord. Chem.*, **64**, 186 (2011).

[53] B.R. Srinivasan, S.Y. Shetgaonkar, N.N. Ghosh. *J. Coord. Chem.*, **64**, 1113 (2011).

[54] Y. Abdollahian, J.L. Hauser, D.L. Rogow, A.G. Oliver, S.R. Oliver. *Dalton Trans.*, **41**, 12630 (2012).

[55] D. Saha, R. Sen, T. Maity, S. Koner. *Dalton Trans.*, **41**, 7399 (2012).

[56] J.M. Taylor, R. Vaidhyanathan, S.S. Iremonger, G.K. Shimizu. *J. Am. Chem. Soc.*, **134**, 14338 (2012).

[57] L.-D. Wang, F. Tao, M.-L. Cheng, Q. Liu, W. Han, Y.-J. Wu, D.-D. Yang, L.-J. Wang. *J. Coord. Chem.*, **65**, 923 (2012).
[58] L.J. Farrugia. *J. Appl. Crystallogr.*, **32**, 837 (1999).
[59] G.M. Sheldrick. *SHELXS-97 and SHELXL-97*, University of Göttingen, Göttingen (1997).
[60] M.L. Chen, S.Y. Mao, Z.H. Zhou. *Inorg. Chim. Acta*, **376**, 671 (2011).
[61] M.L. Chen, F. Yang, Z.H. Zhou. *Polyhedron*, **47**, 60 (2012).
[62] K. Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part B*, 6th edn, pp. 69–73, Wiley, New York (2009).