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A series of new lanthanoid thioarsenates: insights into the influence of lanthanide contraction on the formation of new lanthanoid thioarsenates†

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A series of new lanthanoid thioarsenates $[\text{Ln}(\text{teta})(\mu-\eta^1:\eta^2:\eta^1-\text{As}^{\text{III}}\text{S}_3)]_n$ (Ln = Ce (**1a**), Pr (**1b**), Nd (**1c**), and Sm (**1d**); tetra = triethylenetetramine) and $[\text{Ln}(\text{teta})(\text{en})(\mu-\eta^1:\eta^1-\text{As}^{\text{V}}\text{S}_4)]_n$ (Ln = La (**2a**), Ce (**2b**), Pr (**2c**), and Nd (**2d**); en = ethylenediamine) were prepared by the solvothermal reaction of K_3AsO_3 , S, LnCl_3 and organic amines and structurally characterized. Compounds **1a–d** crystallise in the orthorhombic space group *Aba2* and display 1-D neutral chains $[\text{Ln}(\text{teta})(\mu-\eta^1:\eta^2:\eta^1-\text{As}^{\text{III}}\text{S}_3)]_n$, which represent the first examples of 1-D organic hybrid lanthanoid sulfides built up from trigonal-pyramidal $[\text{As}^{\text{III}}\text{S}_3]^{3-}$ acting as tetradentate bridging ligands to interlink $[\text{Ln}(\text{teta})]^{3+}$ ions, while compounds **2a–d** crystallise in the orthorhombic space group *P2₁2₁2₁* and consist of other 1-D neutral chains $[\text{Ln}(\text{teta})(\text{en})(\mu-\eta^1:\eta^1-\text{As}^{\text{V}}\text{S}_4)]_n$, which are built up from the linkages of the tetrahedral $[\text{As}^{\text{V}}\text{S}_4]^{3-}$ ion and the $[\text{Ln}(\text{teta})(\text{en})]^{3+}$ ion. To learn more about the influence of lanthanide contraction on the formation of lanthanoid thioarsenates, three organic hybrid lanthanoid thioarsenates $[\text{Ln}(\text{teta})(\text{en})(\mu-\eta^1:\eta^1-\text{As}^{\text{V}}\text{S}_4)]_n$ (Ln = Dy (**3a**), Ho (**3b**), and Tm (**3c**)) with the neutral molecular structure type in the monoclinic centrosymmetric space group *P2₁/c* are also presented. Their optical and magnetic properties have been investigated, and density functional theory calculations of **1a** and **2a** have also been performed.

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Introduction

Lanthanoid chalcogenides are of great interest in inorganic solid chemistry and materials science due to their fascinating architectures and potential applications such as optical fibers, semiconductors, magnetism, luminescence and nonlinear optical properties in an extended infrared region.¹ The incorporation of lanthanide metal elements (Ln) into chalcogenidometalate frameworks is a feasible and promising route for preparation of a new class of lanthanoid chalcogenides,² which are capable of not only enhancing their structural diver-

sity, but also integrating the electronic, optical, and magnetic properties of lanthanide ions with various physical properties of the host chalcogenidometalate frameworks, rendering them potentially suitable for application in different technical fields. Arsenic is of specific interest since the As^{3+} ion often shows the asymmetric fundamental units of $[\text{AsQ}_x]$ (Q = chalcogenides, $x = 3, 4$) with stereochemically active lone pairs, which could induce the formation of non-centrosymmetric structures, leading to interesting important properties, such as nonlinear optics.³ For instance, the non-centrosymmetric LiAsS_2 ^{3e} and $\gamma\text{-NaAsSe}_2$ ^{3b} built up from corner-sharing $[\text{As}^{\text{III}}\text{Q}_3]^{3+}$ (Q = S, Se) trigonal pyramids, which display a strong nonlinear optical response (NLO), were achieved by the alkali metal polychalcogenide flux method. The non-centrosymmetric $\text{A}_3\text{Ta}_2\text{AsS}_{11}$ (A = K and Rb)^{3a} contain a 1-D non-centrosymmetric $[\text{Ta}_2\text{AsS}_{11}^{3-}]_n$ chain constructed by the linkages of $[\text{AsS}_3]^{3-}$ trigonal pyramids and asymmetric $[\text{Ta}_2\text{S}_{11}]^{6-}$ units, which were prepared by similar flux methods at 550 °C using $\text{A}_2\text{S}/\text{Ta}/\text{As}/\text{S}$ mixtures. As expected, the integration of Ln atoms into chalcogenidoarsenate backbones may produce a new class of lanthanoid chalcogenidoarsenates with new structures and unexpected properties. So far, significant work on the polychalcogenide flux syntheses of lanthanoid chalcogenidoarsenates has been reported,⁴ but they mostly exhibit centrosym-

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metric structures, mainly because the As^{3+} ion is easily oxidized to the As^{5+} ion in the oxidizing environment of a higher basicity flux. Therefore, the syntheses of non-centrosymmetric lanthanoid chalcogenidoarsenates remain among the most attractive and challenging tasks.

Moreover, lanthanoid chalcogenides were mostly prepared by traditional flux methods at high temperatures,^{1–4} which could result from the $\text{O}_2/\text{H}_2\text{O}$ sensitivity of these materials in the solvents and soft Lewis basic Q atoms (Q = S, Se, Te) difficultly coordinated to hard Lewis acidic Ln^{3+} cations, but one of the goals of materials science is to achieve novel advanced functional materials at quite a low temperature. The solvothermal method performed in a limited sealed reactor at low temperatures can not only reduce some unfavorable influence, but also be suitable for crystal growth and the control of crystal sizes. Recently, we have preliminarily investigated the solvothermal syntheses of lanthanide chalcogenides in organic amine solutions, and successfully achieved some excited lanthanide sulfides⁵ with interesting supertetrahedral cluster $[\text{In}_4\text{S}_{10}]^{8-}$, dimeric $[\text{Ge}_2\text{S}_6]^{4-}$ or $[\text{Sn}_2\text{Q}_6]^{4-}$ (Q = S, Se), and simple tetrahedral $[\text{Sb}^{\text{V}}\text{S}_4]^{3-}$ or $[\text{As}^{\text{V}}\text{S}_4]^{3-}$ anions as soft Lewis basic ligands coordinated to hard Lewis acidic Ln^{3+} ions *via* Ln–Q bonds. These anions based on tetrahedral $[\text{MQ}_4]$ (M = In, Ge, Sn, Sb) units usually have a symmetrical center, symmetrical plane, and an improper axis of rotation of the order n ,⁶ resulting in the centrosymmetric structures. However, the solvothermal synthesis of non-centrosymmetric lanthanoid chalcogenidometalates is very difficult and remains a great attractive and challenging goal. To increase the structural diversity with important physico-chemical properties, new types of non-centrosymmetric lanthanoid chalcogenidometalates with an acentric building unit are often desired. Herein we report a series of non-centrosymmetric lanthanoid thioarsenates $[\text{Ln}(\text{teta})(\mu-\eta^1:\eta^2:\eta^1\text{-As}^{\text{III}}\text{S}_3)]_n$ {Ln = Ce (**Ia**), Pr (**Ib**), Nd (**Ic**) and Sm (**Id**)} and $[\text{Ln}(\text{teta})(\text{en})(\mu-\eta^1:\eta^1\text{-As}^{\text{V}}\text{S}_4)]_n$ {Ln = La (**Iia**), Ce (**Iib**), Pr (**Iic**), and Nd (**Iid**)}, where acentric $[\text{As}^{\text{III}}\text{S}_3]^{3-}/[\text{As}^{\text{V}}\text{S}_4]^{3-}$ anions act as bridging ligands to link lanthanide complexes $[\text{Ln}(\text{teta})]^{3+}/[\text{Ln}(\text{teta})(\text{en})]^{3+}$ into 1-D non-centrosymmetric chains. Both **Ia–d** and **Iia–d** represent the rare examples of non-centrosymmetric lanthanoid chalcogenidometalates under solvothermal conditions. To gain insight into the influence of lanthanide contraction on the formation of lanthanoid thioarsenates, three centrosymmetric lanthanoid thioarsenates $[\text{Ln}(\text{teta})(\text{en})\text{As}^{\text{V}}\text{S}_4]$ [Ln = Dy (**IIia**), Ho (**IIib**), and Tm (**IIic**)] are also presented.

Experimental

General remarks

All analytical grade chemicals were obtained commercially and used without further purification. IR spectra were obtained from a powdered sample pelletized with KBr on an ABB Bomen MB 102 series IR spectrophotometer in the range of 400–4000 cm^{-1} . Elemental analyses (C, H, N) were performed on an Elemental Vario EL III analyzer. Room-temperature

optical diffuse reflectance spectra of the powdered samples were obtained on a Shimadzu UV-3150 spectrometer. Variable temperature susceptibility measurements were carried out in the temperature range 2–300 K at a magnetic field of 1 kOe on polycrystalline samples with a Quantum Design MPMS XL-5 SQUID magnetometer. All the magnetic susceptibility data were corrected for magnetization of the sample holder and for diamagnetic contribution estimated from Pascal's constants. PXRD patterns were obtained using a Bruker D8 Advance XRD diffractometer with Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$).

Synthesis of $[\text{Ce}(\text{teta})(\mu-\eta^1:\eta^2:\eta^1\text{-As}^{\text{III}}\text{S}_3)]_n$ (**Ia**)

The reagents of CeCl_3 (0.0160 g), S (0.0223 g), K_3AsO_3 (0.0143 g) and *teta* (2.0 mL) were placed in a thick Pyrex tube (*ca.* 20 cm long). The sealed tube was heated at 170 °C for 10 days to obtain yellow crystals. The crystals were washed with ethanol, dried and stored under vacuum (43% yield based on K_3AsO_3). Anal. calcd for **Ia**, $\text{C}_6\text{H}_{18}\text{AsCeN}_4\text{S}_3$, C 18.32%, H 4.61%, N 14.24%, found: C 18.27%, H 4.68%, N 14.30%. IR (cm^{-1}): 3323(m), 3120(m), 2939(w), 2863(m), 1559(m), 1458(m), 1378(w), 1320(m), 1263(w), 1220(w), 1111(m), 1002(s), 945(s), 894(s), 865(s), 836(w), 533(m), 410(m).

Synthesis of $[\text{Pr}(\text{teta})(\mu-\eta^1:\eta^2:\eta^1\text{-As}^{\text{III}}\text{S}_3)]_n$ (**Ib**)

The green crystals of **Ib** were prepared similarly from PrCl_3 (yield 64% based on K_3AsO_3). Anal. calcd for **Ib**, $\text{C}_6\text{H}_{18}\text{AsN}_4\text{PrS}_3$, C 18.29%, H 4.60%, N 14.22%, found: C 18.31%, H 4.65%, N 14.27%. IR (cm^{-1}): 3315(w), 3134(m), 2939(w), 2831(m), 1559(m), 1451(m), 1364(w), 1306(m), 1255(m), 1190(m), 1097(m), 1024(w), 1009(m), 945(vs), 887(s), 865(s), 829(w), 591(w), 526(s), 410(m).

Synthesis of $[\text{Nd}(\text{teta})(\mu-\eta^1:\eta^2:\eta^1\text{-As}^{\text{III}}\text{S}_3)]_n$ (**Ic**)

The blue crystals of **Ic** were prepared similarly from NdCl_3 (yield 71% based on K_3AsO_3). Anal. calcd for **Ic**, $\text{C}_6\text{H}_{18}\text{AsN}_4\text{NdS}_3$, C 18.13%, H 4.56%, N 14.10%, found: C 18.20%, H 4.62%, N 14.15%. IR (cm^{-1}): 3344(m), 3192(m), 2918(w), 2852(m), 1544(m), 1451(m), 1298(w), 1104(m), 1017(w), 952(s), 894(m), 880(m), 605(w), 540(m), 403(m).

Synthesis of $[\text{Sm}(\text{teta})(\mu-\eta^1:\eta^2:\eta^1\text{-As}^{\text{III}}\text{S}_3)]_n$ (**Id**)

The light yellow crystals of **Id** were prepared similarly from SmCl_3 (yield 42% based on K_3AsO_3). Anal. calcd for **Id**, $\text{C}_6\text{H}_{18}\text{AsN}_4\text{S}_3\text{Sm}$, C 15.41%, H 3.88%, N 11.98%, found: C 15.48%, H 3.95%, N 12.08%. IR (cm^{-1}): 3323(w), 3134(m), 2939(w), 2860(m), 1581(m), 1458(m), 1328(w), 1255(w), 1205(w), 1097(w), 1009(m), 945(s), 901(s), 865(m), 836(w), 597(w), 547(m), 432(m).

Synthesis of $[\text{La}(\text{teta})(\text{en})(\mu-\eta^1:\eta^1\text{-As}^{\text{V}}\text{S}_4)]_n$ (**Iia**)

The reagents of LaCl_3 (0.0125 g), S (0.0224 g), K_3AsO_3 (0.0140 g), *teta* (1.5 mL) and *en* (0.5 mL) were placed in a thick Pyrex tube (*ca.* 20 cm long). The sealed tube was heated at 170 °C for 4 days to obtain colorless crystals. The crystals were washed with ethanol, dried and stored under vacuum (67% yield based on K_3AsO_3). Anal. calcd for **Iia**, $\text{C}_8\text{H}_{26}\text{AsLaN}_6\text{S}_4$,

C 21.25%, H 5.80%, N 18.58%, found: C 21.17%, H 5.92%, N 18.65%. IR (cm⁻¹): 3278(m), 3207(m), 3120(m), 2911(m), 2860(m), 1574(s), 1320(m), 1140(m), 1046(s), 901(s), 800(m), 591(m), 468(w), 410(s).

Synthesis of [Ce(teta)(en)(μ-η¹:η¹:η¹-As^VS₄)]_n (**IIb**)

The yellow crystals of **IIb** were prepared by a similar method to that used in the synthesis of the crystals of **IIa** except that LaCl₃ was replaced by CeCl₃ (62% yield based on K₃AsO₃). Anal. calcd for **IIb**, C₈H₂₆AsCeN₆S₄, C 21.19%, H 5.78%, N 18.53%, found: C 21.23%, H 5.84%, N 18.60%. IR (cm⁻¹): 3323(m), 3214(m), 3185(m), 3105(m), 2925(m), 2845(m), 1544(s), 1328(m), 1097(m), 1046(m), 996(m), 945(w), 808(w), 707(w), 591(m), 410(s).

Synthesis of [Pr(teta)(en)(μ-η¹:η¹:η¹-As^VS₄)]_n (**IIc**)

The green crystals of **IIc** were prepared by a similar method to that used in the synthesis of the crystals of **IIa** except that LaCl₃ was replaced by PrCl₃ (75% yield based on K₃AsO₃). Anal. calcd for **IIc**, C₈H₂₆AsN₆PrS₄, C 21.15%, H 5.77%, N 18.50%, found: C 21.09%, H 5.83%, N 18.46%. IR (cm⁻¹): 3301(m), 3265(m), 3207(m), 2932(m), 2832(m), 1537(s), 1378(w), 1320(s), 1097(m), 1039(w), 981(w), 793(w), 591(m), 424(s).

Synthesis of [Nd(teta)(en)(μ-η¹:η¹:η¹-As^VS₄)]_n (**IId**)

The cerulean crystals of **IId** were prepared by a similar method to that used in the synthesis of the crystals of **IIa** except that LaCl₃ was replaced by NdCl₃ (68% yield based on K₃AsO₃). Anal. calcd for **IId**, C₈H₂₆AsN₆NdS₄, C 21.00%, H 5.73%, N 18.37%, found: C 21.07%, H 5.81%, N 18.42%. IR (cm⁻¹): 3308(m), 3235(m), 3112(m), 2911(m), 2840(m), 1595(s), 1443(w), 1328(w), 1255(w), 1125(s), 1075(s), 1017(s), 974(m), 931(m), 728(w), 612(s), 576(m), 468(m), 431(s).

Synthesis of [Dy(teta)(en)As^VS₄] (**IIIa**)

The light yellow crystals of **IIIa** were prepared by a similar method to that used in the synthesis of the crystals of **IIa** except that LaCl₃ was replaced by DyCl₃ (63% yield based on K₃AsO₃). Anal. calcd for **IIIa**, C₈H₂₆AsDyN₆S₄, C 20.19%, H 5.51%, N 17.66%, found: C 20.23%, H 5.62%, N 17.72%. IR (cm⁻¹): 3250(m), 3192(m), 3120(m), 2925(m), 2878(m), 1566(s), 1509(w), 1458(m), 1328(w), 1263(w), 1162(w), 1140(m), 1089(m), 1031(s), 945(s), 800(w), 605(m), 511(m), 418(s).

Synthesis of [Ho(teta)(en)As^VS₄] (**IIIb**)

The red crystals of **IIIb** were prepared by a similar method to that used in the synthesis of the crystals of **IIa** except that LaCl₃ was replaced by HoCl₃ (71% yield based on K₃AsO₃). Anal. calcd for **IIIb**, C₈H₂₆AsHoN₆S₄, C 20.09%, H 5.48%, N 17.57%, found: C 20.14%, H 5.52%, N 17.61%. IR (cm⁻¹): 3250(m), 3192(m), 3112(m), 2911(m), 2867(m), 1581(m), 1458(m), 1328(w), 1285(m), 1162(w), 1182(m), 1017(s), 938(s), 808(w), 605(m), 519(m), 410(s).

Synthesis of [Tm(teta)(en)As^VS₄] (**IIIc**)

The light yellow crystals of **IIIc** were prepared by a similar method to that used in the synthesis of the crystals of **IIa** except that LaCl₃ was replaced by TmCl₃ (51% yield based on K₃AsO₃). Anal. calcd for **IIIc**, C₈H₂₆AsN₆S₄Tm, C 16.61%, H 4.53%, N 14.53%, found: C 16.65%, H 4.60%, N 14.57%. IR (cm⁻¹): 3250(m), 3200(m), 3112(m), 2932(m), 2867(m), 1566(m), 1451(m), 1343(m), 1270(m), 1169(w), 1132(m), 1024(s), 945(s), 808(w), 605(m), 489(m), 414(s).

X-ray crystallography

Single-crystal X-ray diffraction data for all compounds were collected on a Rigaku Mercury CCD diffractometer using a ω-scan method with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at 296(2) K. Routine Lorentz polarization and absorption corrections were applied using the multi-scan technique. The structures of all compounds were solved by direct methods of SHELXS-97⁷ and refined by full-matrix least-squares methods on F² using the SHELXL-97 program package.⁸ Positions of H atoms attached to the C and N atoms in all compounds were geometrically placed and H atoms were refined isotropically as a riding mode using the default SHELXTL parameters. A summary of crystallographic data is listed in Table 1. 1033469–1033479 contain the supplementary crystallographic data for this paper.

Results and discussion

Synthetic aspects

The reported chalcogenidoarsenates can be obtained by using binary arsenic chalcogenides, arsenic chalcogenide salt, or As₂O₃ as the As source in the presence of an organic amine under solvothermal conditions,⁹ but K₃AsO₃ salt has not been used in the solvothermal reaction system for chalcogenidoarsenates to date. In this work, we attempted to use K₃AsO₃ as the starting material for the synthesis of the lanthanoid thioarsenates, and successfully synthesized a series of non-centrosymmetric lanthanoid thioarsenates [Ln(teta)(μ-η¹:η²:η¹-As^{III}S₃)]_n {Ln = Ce (**Ia**), Pr (**Ib**), Nd (**Ic**), and Sm (**Id**)}, [Ln(teta)(en)(μ-η¹:η¹:η¹-As^VS₄)]_n {Ln = La (**IIa**), Ce (**IIb**), Pr (**IIc**), and Nd (**IId**)} and three centrosymmetric lanthanoid thioarsenates [Ln(teta)(-en)-As^VS₄] [Ln = Dy (**IIIa**), Ho (**IIIb**), and Tm (**IIIc**)], where the S²⁻ anion is produced by the organic amine inducing the disproportionation of S powder.^{8b} K₃AsO₃ was dissolved in a tetra alkaline solution to give the pyramidal [AsS₃]³⁻ anion in **Ia–d**, which was derived from the [AsO₃]³⁻ anion by replacing three O²⁻ ions with three S²⁻ ions, while the [AsO₃]³⁻ anion is converted into the tetrahedral [As^VS₄]³⁻ anion of both **IIa–d** and **IIIa–c** by oxidation and substitution processes in a mixed solvent of en and tetra. Compared with the pure tetra solution under solvothermal conditions, the en solution shows stronger basicity and has the tendency to be oxidized to As⁵⁺ ions in the presence of Ln³⁺ ions. Such a phenomenon is also observed in other lanthanoid thioarsenates {[Eu(en)₃(As^VS₄)] and [Eu(teta)(en)(As^VS₄)]},^{5e} and lanthanoid thioantimonates such as [Ln(en)₄]-

Table 1 Crystallographic data for all compounds

	Ia	Ib	Ic	Id	IIa	IIb
Formula	C ₆ H ₁₈ AsCeN ₄ S ₃	C ₆ H ₁₈ AsN ₄ PrS ₃	C ₆ H ₁₈ AsN ₄ NdS ₃	C ₆ H ₁₈ AsN ₄ S ₃ Sm	C ₈ H ₂₆ AsLaN ₆ S ₄	C ₈ H ₂₆ AsCeN ₆ S ₄
Fw	457.46	458.25	461.58	467.70	548.42	549.63
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	<i>Aba2</i>	<i>Aba2</i>	<i>Aba2</i>	<i>Aba2</i>	<i>P2₁2₁2₁</i>	<i>P2₁2₁2₁</i>
<i>a</i> /Å	19.7580(5)	19.7203(5)	19.648(4)	19.4659(18)	8.3601(2)	8.3413(2)
<i>b</i> /Å	9.6623(2)	9.6404(2)	9.625(3)	9.5700(9)	11.2089(3)	11.1822(3)
<i>c</i> /Å	14.9521(4)	14.9599(4)	14.947(3)	14.7915(14)	19.8455(5)	19.7987(5)
<i>V</i> /Å ³	2854.47(12)	2844.05(12)	2826.9(11)	2755.5(4)	1859.67(8)	1846.71(8)
<i>Z</i>	8	8	8	8	4	4
<i>T</i> /K	296(2)	296(2)	296(2)	296(2)	296(2)	296(2)
Calcd density/Mg m ^{−3}	2.129	2.141	2.169	2.255	1.959	1.977
<i>F</i> (000)	1768	1776	1784	1800	1080	1084
2θ(max.)/°	50.16	50.20	56.72	50.18	53.00	50.18
Total reflns collected	3387	3365	11 560	5148	5938	5011
Unique reflns	2265	1647	3376	2131	3574	3054
No. of parameters	137	137	137	137	182	181
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.0283	0.0304	0.0186	0.0222	0.0279	0.0274
w <i>R</i> ₂ (all data)	0.0597	0.0595	0.0401	0.0540	0.0477	0.0488
GOOF on <i>F</i> ²	1.023	1.023	1.109	1.086	1.017	1.000
Largest diff. peak and hole [e Å ³]	0.548 and −0.822	0.958 and −0.928	0.371 and −0.974	1.291 and −0.864	0.503 and −0.483	0.520 and −0.532
Flack parameters	0.320(17)	0.48(3)	0.024(9)	0.031(15)	0.165(15)	0.322(17)
	IIc	IId	IIIA	IIIB	IIIC	
Formula	C ₈ H ₂₆ AsN ₆ PrS ₄	C ₈ H ₂₆ AsN ₆ NdS ₄	C ₈ H ₂₆ AsDyN ₆ S ₄	C ₈ H ₂₆ AsHoN ₆ S ₄	C ₈ H ₂₆ AsN ₆ S ₄ Tm	
Fw	550.42	553.75	572.01	574.44	578.44	
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	
Space group	<i>P2₁2₁2₁</i>	<i>P2₁2₁2₁</i>	<i>P2₁/c</i>	<i>P2₁/c</i>	<i>P2₁/c</i>	
<i>a</i> /Å	8.3354(2)	8.491(10)	9.6438(5)	9.5522(14)	9.5588(6)	
<i>b</i> /Å	11.1590(2)	11.211(13)	13.1563(7)	13.0616(18)	13.0353(8)	
<i>c</i> /Å	19.7264(4)	19.69(2)	14.5845(8)	14.483(2)	14.4749(8)	
β/°	90	90	97.4360(10)	97.604(2)	97.6090(10)	
<i>V</i> /Å ³	1834.85(7)	1874(4)	1834.87(17)	1791.1(4)	1787.72(19)	
<i>Z</i>	4	4	4	4	4	
<i>T</i> /K	296(2)	296(2)	296(2)	296(2)	296(2)	
Calcd density/Mg m ^{−3}	1.993	1.962	2.071	2.130	2.149	
<i>F</i> (000)	1088	1092	1116	1120	1128	
2θ(max.)/°	50.20	52.98	53.00	50.20	50.20	
Total reflns collected	4451	7881	13 540	10 397	12 751	
Unique reflns	2638	3620	3680	3135	3110	
No. of parameters	182	182	181	181	182	
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.0290	0.0200	0.0215	0.0251	0.0192	
w <i>R</i> ₂ (all data)	0.0573	0.0688	0.0844	0.0639	0.0458	
GOOF on <i>F</i> ²	1.035	1.183	1.162	1.016	1.048	
Largest diff. peak and hole [e Å ³]	1.247 and −0.951	0.722 and −1.485	0.769 and −0.891	1.308 and −1.133	0.771 and −0.552	
Flack parameters	0.14(2)	0.111(15)				

Sb^VS₄·0.5en (Ln = Eu, Dy, Yb)¹⁰ and [Ln(en)₃(H₂O)_x(SbS₄)] (Ln = La, x = 0; Ln = Nd, x = 1).¹⁰ So far, to the best of our knowledge, no 1–3-D organic hybrid lanthanoid thioantimonates(III) containing the [As^{III}S₃]^{3−} unit under solvothermal conditions have been reported. So **Ia–d** are the rare examples of 1-D lanthanoid thioarsenates with the non-condensed [As^{III}S₃]^{3−} unit containing the As³⁺ ion under solvothermal conditions.

Crystal structure

Descriptions of Ia–d. **Ia–d** have the general formula [Ln(teta)(μ-η¹:η²:η¹-As^{III}S₃)]_n and are isomorphic, so we only discussed the structure of **Ia** (Fig. 1a). **Ia** crystallizes in the orthorhombic space group of *Aba2* and consists of 1-D neutral chains [Ce(teta)(μ-η¹:η²:η¹-As^{III}S₃)]_n built up from [Ce(teta)]³⁺

fragments bridged by [As^{III}S₃]^{3−} anions with a Ce...Ce distance of 5.4744(4) Å (Fig. 2a). Each As³⁺ ion is coordinated to three S^{2−} ions to give a pyramidal [As^{III}S₃]^{3−} unit. The As–S bond distances and S–As–S bond angles are in the typical range of those for the well-known pyramidal [As^{III}S₃]^{3−} unit. Each Ce³⁺ ion is chelated by one tetradentate teta ligand and coordinated by four S atoms from two [As^{III}S₃]^{3−} units to form a distorted bicapped trigonal prism (Fig. 1b). The Ln–N bond distances decrease from Ce to Sm, as expected from the lanthanide contraction. The bond lengths of Ce–S (2.9419(19)–2.9827(17) Å), Pr–S (2.921(3)–2.973(2) Å), Nd–S (2.8313(8)–2.9624(9) Å), and Sm–S (2.8044(12)–2.9293(13) Å) are in agreement with those observed in other multinary lanthanoid sulfides.¹¹

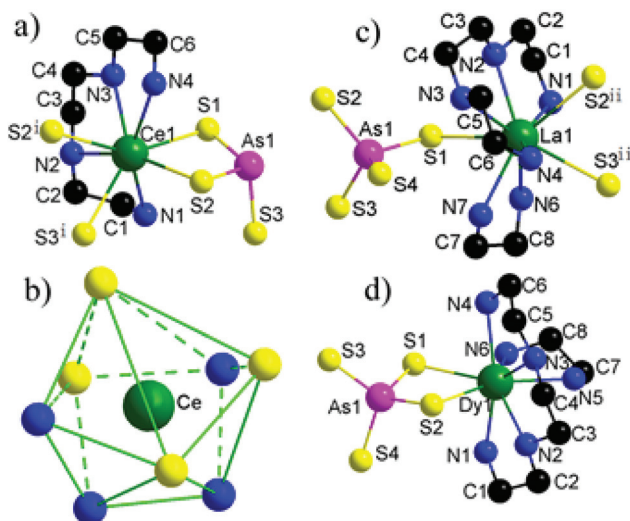


Fig. 1 Crystal structures of Ia (a), IIa (c) and IIIa (d) with the labeling scheme. (b) Coordination environment of the Ce^{3+} ion. All H atoms are omitted for clarity. Symmetry operation: (i) $1.5 - x, 0.5 + y, z$; (ii) $-1 + x, y, z$.

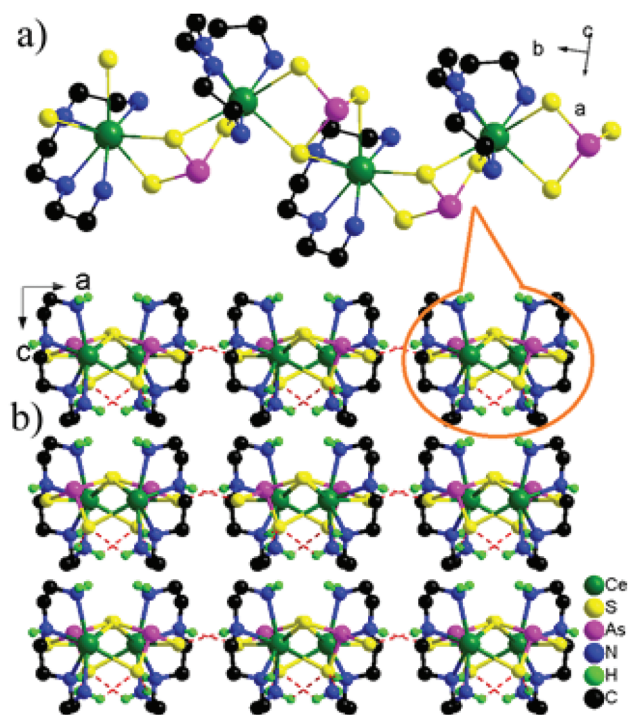


Fig. 2 (a) 1-D polar $[\text{Ce}(\text{teta})\text{As}^{\text{III}}\text{S}_3]_n$ chain of Ia, showing the connectivity between acentric $[\text{As}^{\text{III}}\text{S}_3]^{3-}$ anions and $[\text{Ce}(\text{teta})]^{3+}$ groups, (b) the packing of the $[\text{Ce}(\text{teta})\text{As}^{\text{III}}\text{S}_3]_n$ chains in Ia (H atoms on C atoms are omitted for clarity).

The pyramidal $[\text{As}^{\text{III}}\text{S}_3]^{3-}$ anion exhibits an acentric mode due to the As atom containing a 4s lone electron pair. The acentric characteristics of the $[\text{As}^{\text{III}}\text{S}_3]^{3-}$ anion can be transferred to the $[\text{Ce}(\text{teta})]^{3+}$ group *via* Ce–S bonds, resulting in an

acentric $[\text{Ce}(\text{teta})]^{3+}$ group. The acentric $[\text{As}^{\text{III}}\text{S}_3]^{3-}$ anions combine with acentric $[\text{Ce}(\text{teta})]^{3+}$ groups to form the 1-D non-centrosymmetric chain $[\text{Ce}(\text{teta})\text{As}^{\text{III}}\text{S}_3]_n$. These chains are connected *via* N–H...S hydrogen bonds forming a layered arrangement parallel to the (010) plane. Such layers are arranged in parallel with an interlayer distance of about 8.9 Å (Fig. 2b).

The $[\text{As}^{\text{III}}\text{S}_3]^{3-}$ anion with high negative charge density usually shows the characteristic condensation under solvothermal conditions, resulting in a lot of new polynuclear anions, as exemplified by dimeric $[\text{As}_2\text{S}_5]^{4-}$, cyclic $[\text{As}_3\text{S}_6]^{3-}$ or $[\text{As}_4\text{S}_8]^{4-}$, 1-D chains $[\text{As}_4\text{S}_7]^{2-}$ or $[\text{AsS}_2]^-$, and 2-D layers $[\text{As}_8\text{S}_{13}]^{2-}$ or $[\text{As}_6\text{S}_{10}]^{2-}$. But the non-condensed $[\text{As}^{\text{III}}\text{S}_3]^{3-}$ anions are relatively rare and the limited examples include $\{[\text{Mn}(\text{phen})]_3(\text{As}^{\text{III}}\text{S}_3)_2\} \cdot \text{H}_2\text{O}$,¹² $\{[\text{Mn}(\text{phen})]_3(\text{As}^{\text{V}}\text{S}_4)(\text{As}^{\text{III}}\text{S}_3)\}_n \cdot n\text{H}_2\text{O}$,¹³ and KCu_2AsS_3 ,¹⁴ where the $[\text{As}^{\text{III}}\text{S}_3]^{3-}$ anion is stabilized by coordinating to transition metal complexes or metal cations. The non-condensed $[\text{As}^{\text{III}}\text{S}_3]^{3-}$ anion bound to a lanthanide complex *via* Ln–S bond under solvothermal conditions is unfamiliar and the only example is $[\text{La}_2(\text{tepa})_2(\mu-\eta^1, \eta^3-\text{AsS}_3)_2]^{5e}$ where the $[\text{AsS}_3]^{3-}$ anion as a $\mu-\eta^1, \eta^3-\text{AsS}_3$ ligand links the complex cation $[\text{La}(\text{tepa})]^{3+}$ into a 0-D neutral centrosymmetric $[\text{La}_2(\text{tepa})_2(\mu-\eta^1, \eta^3-\text{AsS}_3)_2]$ molecule. But no 1-D lanthanoid thioarsenates based on non-condensed $[\text{As}^{\text{III}}\text{S}_3]^{3-}$ anions have been reported to date. So the 1-D $[\text{Ln}(\text{teta})(\mu-\eta^1, \eta^2: \eta^1-\text{As}^{\text{III}}\text{S}_3)]_n$ chains of **Ia–d** are the rare examples of the non-condensed $[\text{As}^{\text{III}}\text{S}_3]^{3-}$ anion combined with a lanthanide complex *via* Ln–S bonds.

Repeated corner-sharing of pyramidal $[\text{AsS}_3]^{3-}$ units produces 1-D non-centrosymmetric pure inorganic thioarsenate chains $[\text{AsS}_2]^-$ that have been observed in LiAsS_2 ^{3e} and $\text{Li}_{0.6}\text{Na}_{0.4}\text{AsS}_2$.^{3e} The pyramidal $[\text{AsS}_3]^{3-}$ anion as the bridging ligand also links a transition metal complex into 1-D non-centrosymmetric chains including $\text{A}_3\text{Ta}_2\text{AsS}_{11}$ (A = K and Rb)^{3a} and $\{[\text{Mn}(\text{phen})]_3(\text{As}^{\text{V}}\text{S}_4)(\text{As}^{\text{III}}\text{S}_3)\}_n \cdot n\text{H}_2\text{O}$.¹³ But no 1-D non-centrosymmetric chains based on the linkages of $[\text{AsS}_3]^{3-}$ anions and lanthanide complexes have been reported, due to the soft Lewis basic S^{2-} ligand difficultly bound to the hard Lewis acidic Ln^{3+} ion. Therefore, **Ia–d** are a new type of 1-D non-centrosymmetric chain of thioarsenates with a lanthanide complex.

Descriptions of IIa–d. **IIa–d** are isomorphic, so the structure of **IIa** is discussed here in detail (Fig. 1c). **IIa** crystallizes in the orthorhombic chiral space group of $P2_12_12_1$. The crystal structure of **IIa** consists of 1-D neutral $[\text{La}(\text{teta})(\text{en})(\mu-\eta^1, \eta^1: \eta^1-\text{As}^{\text{V}}\text{S}_4)]_n$ chains containing the tetrahedral $[\text{As}^{\text{V}}\text{S}_4]^{3-}$ anion (Fig. 3a). The $[\text{As}^{\text{V}}\text{S}_4]^{3-}$ ion acts as the tridentate $\mu-\eta^1, \eta^1: \eta^1-\text{As}^{\text{V}}\text{S}_4$ bridging ligand to link the lanthanide complex $[\text{Ln}(\text{teta})(\text{en})]^{3+}$ ion into the 1-D neutral chain $[\text{La}(\text{teta})(\text{en})(\mu-\eta^1, \eta^1: \eta^1-\text{As}^{\text{V}}\text{S}_4)]_n$. The La^{3+} cation adopts a distorted monocapped square antiprism comprising six N atoms from tetra and en ligands, and three S atoms from two different $[\text{As}^{\text{V}}\text{S}_4]^{3-}$ anions. The La–N bond lengths in the range of 2.651(3)–2.735(4) Å are compared with those in other lanthanum complexes with N donor atoms.^{5e} The La–S bond distances vary from 3.0233(12) to 3.1180(11) Å, which are in agreement with the corresponding values of lanthanum sulfides with S donor atoms.^{5e}

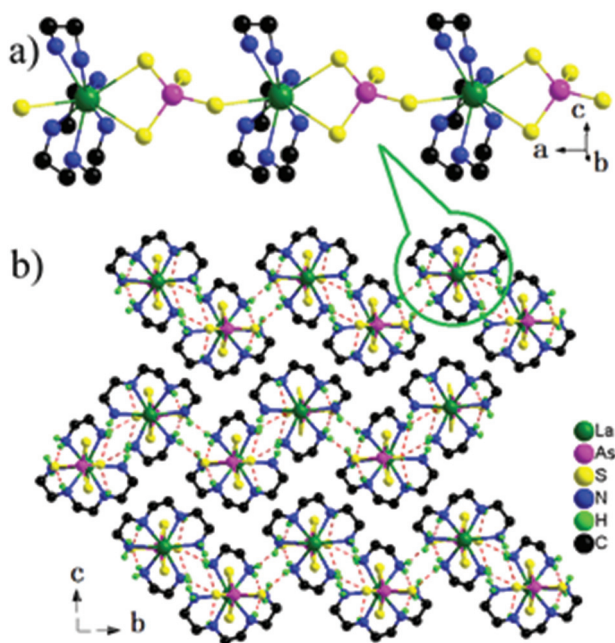


Fig. 3 (a) 1-D chiral $[\text{La}(\text{teta})(\text{en})(\mu\text{-}\eta^1, \eta^2\text{-As}^{\text{VS}}_4)]_n$ chain of **IIa**, (b) the packing of the $[\text{La}(\text{teta})(\text{en})(\mu\text{-}\eta^1, \eta^2\text{-As}^{\text{VS}}_4)]_n$ chains in **IIa** (H atoms on C atoms are omitted for clarity).

The $[\text{As}^{\text{VS}}_4]^{3-}$ anion with different As–S bond distances (2.1493(12)–2.1710(11) Å) is a distorted tetrahedron, as evidenced by the S–As–S angles varying from 105.72(5) to 110.88(6)° deviating from the ideal value of 109.5°. More interestingly, the $[\text{As}^{\text{VS}}_4]^{3-}$ anion and the $[\text{La}(\text{teta})(\text{en})]^{3+}$ fragment in **IIa** have no symmetrical center, symmetrical plane, and improper axis of rotation of the order n , which displays a chiral mode. The combination between chiral $[\text{As}^{\text{VS}}_4]^{3-}$ anions and chiral $[\text{La}(\text{teta})(\text{en})]^{3+}$ fragments leads to a chiral chain $[\text{La}(\text{teta})(\text{en})(\mu\text{-}\eta^1, \eta^2\text{-As}^{\text{VS}}_4)]_n$. A look at the unit cells of these structures reveals that 4 chains (two pairs) are included in each cell. Each pair includes chains of the same chirality but the pairs are of the opposite chirality (Fig. 3b), therefore the bulk material is not chiral. So far, the reported analogous $[\text{Sb}^{\text{VS}}_4]^{3-}$ anion acts as the bridging ligand to the $[\text{Ln}(\text{amine})_x]^{3+}$ fragment to usually form the 1-D centrosymmetric lanthanoid thioantimonates with the centrosymmetric space groups (such as $P2_1/c$,^{10,11a} $Pnma$,¹⁰ and $Pbca$ ^{11d}), for example the 1-D neutral $[\text{Sm}(\text{en})_3(\text{H}_2\text{O})(\mu\text{-Sb}^{\text{VS}}_4)]$ chain^{11a} is built up from the linkages of $[\text{Sb}^{\text{VS}}_4]^{3-}$ anions and $[\text{Sm}(\text{en})_3(\text{H}_2\text{O})]^{3+}$ groups, where the Sb, Sm, O, and two S atoms of one $[\text{Sb}^{\text{VS}}_4]^{3-}$ anion constitute a mirror plane, and two en ligands are mirror images of each other, resulting in a 1-D centrosymmetric structure. Therefore, the 1-D chiral chains constructed by the combination of chiral $[\text{As}^{\text{VS}}_4]^{3-}$ anions and chiral $[\text{La}(\text{teta})(\text{en})]^{3+}$ fragments in **IIa–d** represent a new type within the lanthanoid sulfides.

Descriptions of IIIa–c. **IIIa–c** are isomorphic and are structural isomers of **IIa–d** with the same formula $[\text{Ln}(\text{teta})(\text{en})(\text{As}^{\text{VS}}_4)]$ as they have one unique Ln³⁺ ion, one teta ligand, one

en ligand, and one $[\text{As}^{\text{VS}}_4]^{3-}$ anion in the asymmetric unit (Fig. S1c† and Fig. 1d). Herein, the structure of **IIIa** is discussed in detail. **IIIa** crystallizes in the monoclinic centrosymmetric space group of $P2_1/c$ and displays a neutral $[\text{Dy}(\text{teta})(\text{en})(\text{As}^{\text{VS}}_4)]$ molecule. The Dy³⁺ cation is chelated by one en ligand and one bidentate to form a unsaturated complex $[\text{Dy}(\text{teta})(\text{en})]^{3+}$ ion, which further links the chelating $[\text{As}^{\text{VS}}_4]^{3-}$ anion into a neutral $[\text{Dy}(\text{teta})(\text{en})(\text{As}^{\text{VS}}_4)]$ molecule with a Dy...As distance of 3.6164(5) Å. The Dy³⁺ cation adopts a distorted bicapped trigonal prism comprising six N atoms from teta and en ligands, and two S atoms of one $[\text{As}^{\text{VS}}_4]^{3-}$ anion. The Dy–N (2.499(4)–2.532(4) Å) and Dy–S (2.8129(11)–2.8439(11) Å) bond distances are compared with those observed in the literature.^{11d}

Although the $[\text{Dy}(\text{teta})(\text{en})(\text{As}^{\text{VS}}_4)]$ molecule has no symmetrical center and symmetrical plane, two neighboring molecules are mirror images of each other, resulting in a centrosymmetric structure. A lot of N–H...S hydrogen bonds are found in **IIIa**. The S atoms of $[\text{Dy}(\text{teta})(\text{en})(\text{As}^{\text{VS}}_4)]$ are involved in inter-molecular N–H...S hydrogen bonding with neighboring molecules, leading to a 2-D layer parallel to the (100) plane (Fig. 4). These layers further interact by N–H...S hydrogen bonding to give a 3-D hydrogen bonding network structure (Fig. S3†).

Influence of lanthanide contraction

The Ln³⁺ ions often show variable coordination numbers and geometries, closely related to lanthanide contraction that is used to describe the steady decrease in atomic or ionic radii of the lanthanide elements with increasing nuclear charge in chemistry. In the $\text{LnCl}_3/\text{K}_3\text{AsS}_3/\text{teta}$ system, the reactions from CeCl_3 to SmCl_3 produce lanthanoid thioarsenates with the general formula $[\text{Ln}(\text{teta})(\mu\text{-}\eta^1, \eta^2\text{-As}^{\text{III}}\text{S}_3)]_n$ (Ln = Ce, Pr, Nd, Sm), where the Ln³⁺ ion is bound to four S donor atoms of two different $[\text{As}^{\text{III}}\text{S}_3]^{3-}$ anions and four N donor atoms of one teta ligand, leading to the coordination number of eight. Under similar conditions, we expected that using the heavier Ln³⁺ ions (from EuCl_3 to LuCl_3) in place of the lighter Ln³⁺ ions

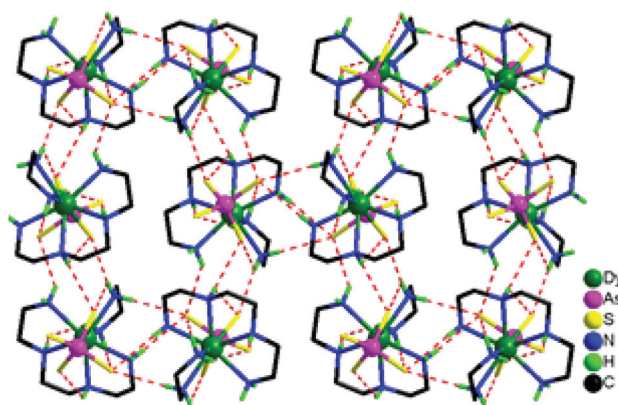


Fig. 4 Part of the crystal structure of **IIIa**, showing that two neighboring molecules are mirror images of each other.

(from CeCl_3 to SmCl_3) would lead to isostructural species **Ia–d**, but we failed to isolate such a product, and only a colloidal product was obtained. This result could be related to the heavier Ln^{3+} ions with smaller ionic radius by the lanthanide contraction effect. For further insights into the influence of lanthanide contraction on the formation of lanthanoid thioarsenates, the introduction of a second organic amine (en) into the $\text{LnCl}_3/\text{K}_3\text{AsS}_3/\text{teta}$ system produces two different types of lanthanoid thioarsenates, namely 1-D chiral chains $[\text{Ln}(\text{teta})(\text{en})(\mu\text{-}\eta^1\text{-}\eta^1\text{-}\text{As}^{\text{VS}}_4)_n]$ ($\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}$) and 0-D neutral molecules $[\text{Ln}(\text{teta})(\text{en})(\text{As}^{\text{VS}}_4)]$ ($\text{Ln} = \text{Dy}, \text{Ho}, \text{Tm}$). The lighter Ln^{3+} ions (La–Nd), which are chelated by one bi-dentate en ligand, tetra-dentate tetra ligand, and one $[\text{As}^{\text{VS}}_4]^{3-}$ anion, leave one coordination site free from the Ln^{3+} ion that is occupied by one S atom of the $[\text{As}^{\text{VS}}_4]^{3-}$ anion, and the final coordination number of Ln^{3+} ions is nine. While the coordination site of heavier Ln^{3+} ions are saturated by six N atoms from en and tetra ligands and two S atoms of the $[\text{As}^{\text{VS}}_4]^{3-}$ anion, the $[\text{As}^{\text{VS}}_4]^{3-}$ ion has no opportunity to bind to the Ln^{3+} center, resulting in the formation of 0-D neutral molecules $[\text{Ln}(\text{teta})(\text{en})(\text{As}^{\text{VS}}_4)]$.

Optical properties

The optical absorption spectra of all compounds were recorded by UV-Vis/NIR diffuse reflectance spectroscopy at room temperature (Fig. 5 and S4†). Their absorption edges are 3.06 eV for **Ia**, 2.84 eV for **Ib**, 2.82 eV for **Ic**, 2.75 eV for **Id**, 2.91 eV for **IIa**, 3.04 eV for **IIb**, 2.91 eV for **IIc**, 3.01 eV for **IId**,

2.92 eV for **IIa**, 2.94 eV for **IIb** and 2.89 eV for **IIc**, which are attributed to the electronic excitation of lanthanoid thioarsenates(III/V). Compared with As_2S_3 of 2.44 eV,^{3e} these compounds show an interesting blue shift of the absorption edge, and a similar phenomenon is also observed in other organic hybrid chalcogenidometalates. The visible color of lanthanoid thioarsenates(III/V) could be closely related to the f–f or d–f transitions of Ln^{3+} ions. Both **Ia** and **Ib** have a broad absorption band of about 2.78 eV originated from the 4f–5d transition of the Ce^{3+} cation with the electronic configuration of $4f^65d^1$.¹⁵ For **Ib** and **Ic**, absorption bands at 2.05 eV, 2.58 eV and 2.73 eV are ascribed to $^3\text{H}_4 \rightarrow ^1\text{D}_2$, $^3\text{H}_4 \rightarrow ^3\text{P}_0$ and $^3\text{H}_4 \rightarrow ^3\text{P}_1$ transitions of the Pr^{3+} cation, respectively.¹⁶ For **Ic** and **IId**, absorption bands at 1.41 eV, 1.53 eV, 1.65 eV, 1.79 eV, 2.08 eV, and 2.34 eV belonged to $^4\text{I}_{9/2} \rightarrow ^4\text{F}_{3/2}$, $^4\text{I}_{9/2} \rightarrow ^4\text{F}_{5/2} + ^2\text{H}_{9/2}$, $^4\text{I}_{9/2} \rightarrow ^4\text{S}_{3/2} + ^4\text{F}_{7/2}$, $^4\text{I}_{9/2} \rightarrow ^4\text{F}_{9/2}$, $^4\text{I}_{9/2} \rightarrow ^4\text{G}_{5/2} + ^2\text{G}_{7/2}$ and $^4\text{I}_{9/2} \rightarrow ^4\text{G}_{7/2} + ^2\text{K}_{13/2}$ transitions of Nd^{3+} cations, respectively.¹⁷ For **Id** and **IIa–d**, there are several characteristic absorptions of the f–f transitions of Sm^{3+} {1.00 eV ($^6\text{H}_{5/2} \rightarrow ^6\text{F}_{7/2}$), 1.14 eV ($^6\text{H}_{5/2} \rightarrow ^6\text{F}_{9/2}$), 1.31 eV ($^6\text{H}_{5/2} \rightarrow ^6\text{F}_{11/2}$)},¹⁶ Dy^{3+} {0.95 eV ($^6\text{H}_{15/2} \rightarrow ^6\text{F}_{11/2} + ^6\text{H}_{9/2}$), 1.12 eV ($^6\text{H}_{15/2} \rightarrow ^6\text{H}_{7/2} + ^6\text{H}_{9/2}$), 1.35 eV ($^6\text{H}_{15/2} \rightarrow ^6\text{F}_{7/2}$) and 1.52 eV ($^6\text{H}_{15/2} \rightarrow ^6\text{F}_{5/2}$)},¹⁶ Ho^{3+} {1.07 eV ($^5\text{I}_8 \rightarrow ^5\text{I}_6$), 1.94 eV ($^5\text{I}_8 \rightarrow ^5\text{F}_5$), 2.29 eV ($^5\text{I}_8 \rightarrow ^5\text{S}_2 + ^5\text{F}_4$), 2.55 eV ($^5\text{I}_8 \rightarrow ^5\text{F}_3$) and 2.73 eV ($^5\text{I}_8 \rightarrow ^5\text{G}_6 + ^5\text{F}_1$)},¹⁸ and Tm^{3+} {1.02 eV ($^3\text{H}_6 \rightarrow ^3\text{H}_5$), 1.58 eV ($^3\text{H}_6 \rightarrow ^3\text{H}_4$), 1.80 eV ($^3\text{H}_6 \rightarrow ^3\text{F}_2$) and 2.67 eV ($^3\text{H}_6 \rightarrow ^1\text{G}_4$)}.¹⁹ But no similar f–f or d–f transitions of **IIa** are observed, which result from the particular electronic configuration of $4f^05d^06s^0$, leading to the colorless **IIa**.

Theoretical studies

To understand further the electronic structures of these lanthanoid thioarsenates, both **Ia** and **IIa** were selected as their representatives to calculate the band structures and the density of states (DOSs) by using the computer code CASTEP. The total and partial DOSs of **Ia** and **IIa** are shown in Fig. 6, the partial DOS of C, N and H atoms near the Fermi level is almost negligible. For **Ia**, the top of the valence band (VB) arises predominantly from S 3p states with a small amount of Ce 5d states, while the bottom of the conduction band (CB) mainly originates from As 4p and Ce 5d states. So the optical absorption of **Ia** can be mainly assigned to the charge transitions from S 3p to As 4p and Ce 5d states. For **IIa**, the VB region below the Fermi level mainly comes from S 3p states and the CB region above the Fermi level is derived mainly from the La 5d and As 4s states. So the band gap absorption of **IIa** can be ascribed to the charge transitions from the S 3p states to La 5d and As 4s states. These results further demonstrate that the soft Lewis basic S atom of the $[\text{As}^{\text{III}}\text{S}_3]^{3-}/[\text{As}^{\text{VS}}_4]^{3-}$ anion is bound to the hard Lewis acidic Ln^{3+} cation *via* the Ln–S bond in the solvents. For **Ia** and **IIa**, the lowest energy of CBs and the highest energy of VBs are located at the same points, and their computational direct band gaps are 2.56 eV for **Ia** and 2.57 eV for **IIa** (Fig. S5†). These values are slightly smaller than the measured optical band gap related to the underestimation of the band gap by the DFT method.²⁰

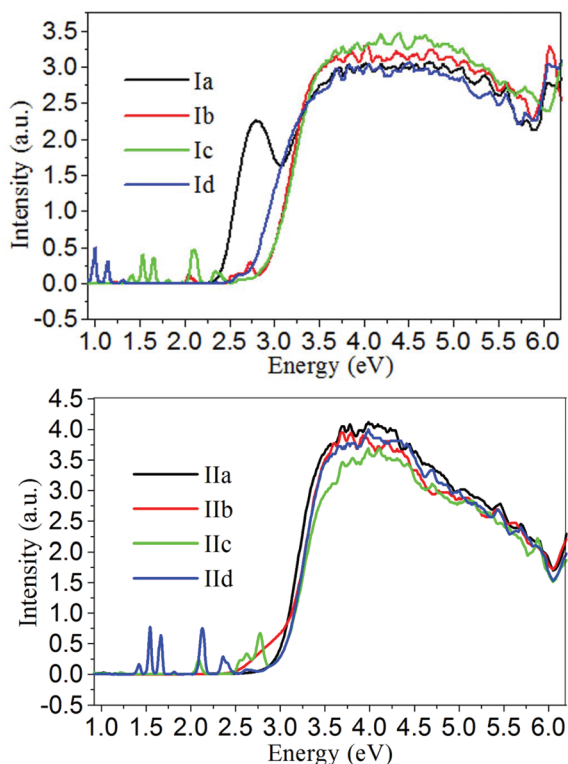


Fig. 5 The solid-state UV-vis absorption spectra of **Ia–d** and **IIa–d**.

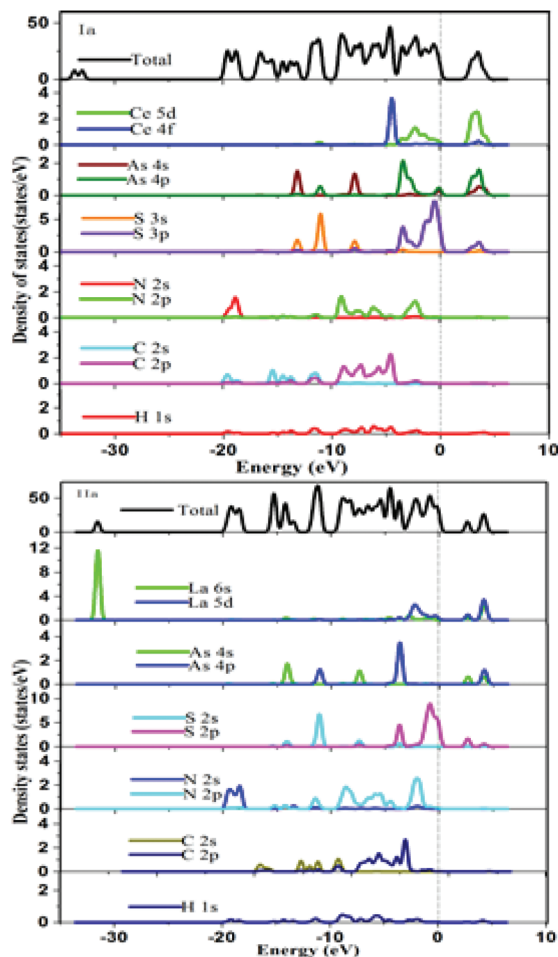


Fig. 6 The total density of states and partial density of states for Ia and IIa. The Fermi level is set at 0 eV (dotted line).

Magnetic properties

Variable-temperature magnetic susceptibilities were determined for **Ib–d** and **IIb–d** in the temperature range of 2 to 300 K under an applied magnetic field of 1 kOe (Fig. 7). The

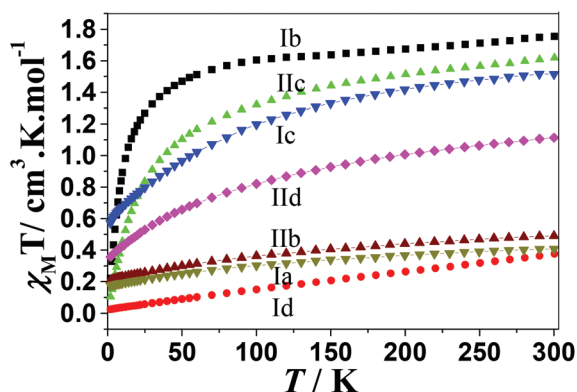


Fig. 7 The plot of $\chi_M T$ versus T for Ia–d and IIb–d.

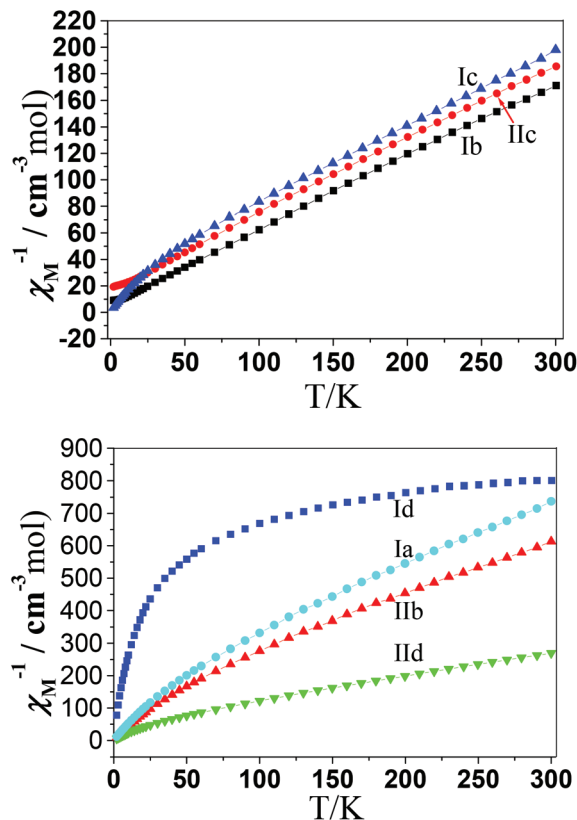


Fig. 8 Plot of χ_M^{-1} versus T for Ia–d and IIb–d.

$\chi_M T$ values at room temperature are $0.41 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ for **Ia**, $1.75 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ for **Ib**, $1.51 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ for **Ic**, $0.37 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ for **Id**, $0.48 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ for **IIb**, $1.62 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ for **IIc** and $1.11 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ for **IId**, which are close to the theoretical value for one non-interacting Ln^{3+} ion ($1.60 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ for Pr^{3+} , $^3\text{H}_4$, $S = 1$, $L = 5$, $g = 4/5$, $J = 4$; $1.64 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ for Nd^{3+} , $^4\text{I}_{9/2}$, $S = 3/2$, $L = 6$, $g = 8/11$, $J = 9/2$; $0.09 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ for Sm^{3+} , $^6\text{H}_{5/2}$, $S = 5/2$, $L = 5$, $g = 2/7$, $J = 5/2$; $0.80 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ for Ce^{3+} , $^2\text{F}_{5/2}$, $S = 1/2$, $L = 3$, $g = 6/7$, $J = 5/2$). With the decrease of temperature, the $\chi_M T$ product exhibits a gradual decrease and then falls to a minimum value of 0.17 , 0.22 , 0.57 , 0.03 , 0.21 , 0.10 and $0.36 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ for **Ib**, **Ic**, **Id**, **IIb**, **IIc** and **IId**, respectively, as a result of the depopulation of the Stark sublevels of the ground J multiplet split by the crystal field and/or the possible magnetic anisotropy present in Ln systems.²¹ The χ_M^{-1} versus T over the entire temperature range for **Ib** and **IIc** can be fitted to the Curie–Weiss law, $\chi_M = C/(T - \theta)$ with the Curie constant $C = 1.90$ and $1.92 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, and the Weiss constant $\theta = -27.08$ and -56.15 , respectively (Fig. 8). But the χ_M^{-1} versus T for **Id** does not obey the Curie–Weiss law that could result from spin–orbit coupling splits of the $^6\text{H}_{5/2}$ ground state.^{1d} **Ia**, **Ic**, **IIb** and **IId** deviate from the Curie–Weiss behavior below 50 K, which has been attributed to crystal field splitting of the $^2\text{F}_{5/2}/^4\text{I}_{9/2}$ ground state.²²

Conclusions

A series of new lanthanoid thioarsenates were synthesized under solvothermal conditions. The pure lower basic tetra solution was found to favor the formation of As^{3+} species in $[\text{Ln}(\text{tetra})(\mu-\eta^1:\eta^2:\eta^1-\text{As}^{\text{III}}\text{S}_3)]_n$ ($\text{Ln} = \text{Ce}, \text{Pr}, \text{Nd}$ and Sm), which represent the first examples of 1-D non-centrosymmetric lanthanoid sulfides constructed by the linkages of acentric trigonal-pyramidal $[\text{As}^{\text{III}}\text{S}_3]^{3-}$ anions and $[\text{Ln}(\text{tetra})]^{3+}$ groups, while the stronger en solution allows the higher valent As^{5+} in 1-D non-centrosymmetric $[\text{Ln}(\text{tetra})(\mu-\eta^1:\eta^2:\eta^1-\text{As}^{\text{V}}\text{S}_4)]_n$ ($\text{Ln} = \text{La}, \text{Ce}, \text{Pr}$ and Nd). This suggests that new non-centrosymmetric lanthanoid thioarsenates with interesting electronic, optical, and magnetic properties were prepared by lower basic organic amines as the reactive solution. Moreover, the lanthanide contraction has a significant effect on the structures of lanthanoid thioarsenates, namely the lighter lanthanides(III) produce 1-D non-centrosymmetric $[\text{Ln}(\text{tetra})(\mu-\eta^1:\eta^2:\eta^1-\text{As}^{\text{III}}\text{S}_3)]_n$ ($\text{Ln} = \text{La}, \text{Ce}, \text{Pr}$ and Nd) and the heavier ones give centrosymmetric $[\text{Ln}(\text{tetra})(\text{en})\text{As}^{\text{V}}\text{S}_4]$ ($\text{Ln} = \text{Dy}, \text{Ho}$, and Tm). The systematic syntheses and structural studies of a series of new lanthanoid thioarsenates would provide possibilities for solvothermal syntheses of other novel lanthanoid thioarsenates with interesting important properties.

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