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Low-temperature thermodynamics of $Ln(Me_2dtc)_3(C_{12}H_8N_2)$ (Me_2dtc = dimethyldithiocarbamate, Ln = La, Pr, Nd, Sm)

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Abstract The heat capacities of $Ln(Me_2dtc)_3(C_{12}H_8N_2)$ (Ln = La, Pr, Nd, Sm, Me_2dtc = dimethyldithiocarbamate) have been measured by the adiabatic method within the temperature range 78–404 K. The temperature dependencies of the heat capacities, $C_{p,m}[La(Me_2dtc)_3(C_{12}H_8N_2)] = 542.097 + 229.576\ X - 27.169\ X^2 + 14.596\ X^3 - 7.135\ X^4$ ($J\ K^{-1}\ mol^{-1}$), $C_{p,m}[Pr(Me_2dtc)_3(C_{12}H_8N_2)] = 500.252 + 314.114\ X - 17.596\ X^2 - 0.131\ X^3 + 16.627\ X^4$ ($J\ K^{-1}\ mol^{-1}$), $C_{p,m}[Nd(Me_2dtc)_3(C_{12}H_8N_2)] = 543.586 + 213.876\ X - 68.040\ X^2 + 1.173\ X^3 + 2.563\ X^4$ ($J\ K^{-1}\ mol^{-1}$) and $C_{p,m}[Sm(Me_2dtc)_3(C_{12}H_8N_2)] = 528.650 + 216.408\ X - 16.492\ X^2 + 12.076\ X^3 + 4.912\ X^4$ ($J\ K^{-1}\ mol^{-1}$), were derived by the least-squares method from the experimental data. The heat capacities of $Ce(Me_2dtc)_3(C_{12}H_8N_2)$ and $Pm(Me_2dtc)_3(C_{12}H_8N_2)$ at 298.15 K were evaluated to be 617.99 and 610.09 $J\ K^{-1}\ mol^{-1}$, respectively. Furthermore, the thermodynamic functions (entropy, enthalpy and Gibbs free energy) have been calculated using the obtained experimental heat capacity data.

Keywords $Ln(Me_2dtc)_3(C_{12}H_8N_2)$ · Adiabatic calorimetry · Heat capacity

Introduction

Over the past few decades significant interest has been focused on the complexes containing the lanthanide-sulfur bond. Special interest in the study of these complexes was aroused because of their diversified applications, such as high pressure lubricants in industry [1, 2], fungicides and pesticides [3], the precursors of ceramics and film [4, 5], accelerators in vulcanization [6]. Inorganic nanocrystals are currently an active field of research in modern materials chemistry. Because of the monomeric and water/air-stable properties, these complexes should be ideal precursors for forming LnS as nanoparticles and bulk materials [7, 8].

Calorimetry is often applied to determine the thermodynamic quantities of many important chemical and physical processes in industrial and scientific research fields [9, 10]. The heat capacity datum plays an important role in theoretical study, application development and industrial production of a compound as a basis of theoretical analysis. In spite of that, there is little reliable experimental data available for these compounds containing lanthanide–sulfur bond.

In the present study, we systematically investigated the heat capacity for $Ln(Me_2dtc)_3(C_{12}H_8N_2)$ (Ln = La, Pr, Nd, Sm, Me_2dtc = dimethyldithiocarbamate) by adiabatic calorimetry. From the temperature dependence of the heat capacities, the thermodynamic functions (entropy, enthalpy, and Gibbs free energy) were derived from these experimental results.

Although promethium is almost non-existent radioactive rare earth elements in the nature, theoretical and applied research on the promethium has been attached great importance. Heat capacities measurements reported in this paper provide the feasibility of predicting the thermodynamic properties for $Pm(Me_2dtc)_3(C_{12}H_8N_2)$.

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Experimental

Materials and analytical methods

Commercially available reagents were used as received without further purification. Elemental analyses of C, H, N were performed on a Vario EL III analyzer. Infrared spectra were obtained from KBr pellets within the region 400–4,000 cm^{-1} on a BEQ VZNDX 550 FTIR spectrometer. The powder X-ray diffraction (PXRD) was recorded on a Rigaku D/Max-2500 diffractometer at 40 kV, 100 mA for a Cu-target tube and a graphite monochromator. The TEM image was recorded using a TEI Technai 20 instrument equipped with a Gatan camera. Thermogravimetric measurements were carried out from room temperature to 900 °C on preweighed samples in hydrostatic air atmosphere using a TA Instruments NETZSCH STA 449C simultaneous TGA–DSC with a heating rate of 5 °C min^{-1}.

$Ln(Me_2dtc)_3(C_{12}H_8N_2)$ preparation and characterization

The samples used in the present measurements were prepared according to the literature [11]. $LnCl_3{\cdot}nH_2O$ (Ln = La, Pr, Nd, Sm, $n = 3$–6), $NaMe_2dtc$ and phen·H_2O (molar ratio = 1/3/1) were dissolved independently in a minimal amount of anhydrous ethanol. A mixed alcoholic solution of phen·H_2O and $NaMe_2dtc$ was dropped slowly to the alcoholic solution of the salt under electromagnetic stirring. The reaction mixture was allowed to stand for 1 h and filtered. The crude product was rinsed three times by a small amount of absolute ethanol portions, followed by purifying with dichloromethane. The final product was obtained and kept in a vacuum over P_4O_{10} to dry for use. The complexes are identified as the general formula of $Ln(Me_2dtc)_3(C_{12}H_8N_2)$ by chemical and elemental analyses. IR spectrum analysis reveals that Ln^{III} cation has a coordination number of 8 with a distorted tetragonal antiprism geometry. The bidentate dimethyldithiocarbamates ligand and the neutral phenanthroline one fill the coordination sphere.

Synthesis of Nd_2S_3 nanocrystal from $Nd(Me_2dtc)_3(C_{12}H_8N_2)$

The thermostability of $Nd(Me_2dtc)_3(C_{12}H_8N_2)$ was investigated by TG-DTG and TG-DTG was performed under dynamic atmosphere of high purity N_2 with a heating rate of 5 °C min. The decomposition of the complex was further investigated by thermolysis experiment. The $Nd(Me_2dtc)_3(C_{12}H_8N_2)$ precursor was heated at 500 °C under tube furnace in high purity N_2 atmosphere in a temperature programming rate of 25 °C min^{-1}. Subsequently, the mixture was heated at 1,000 °C for 6 h. The final product from the thermolysis was characterized by XRD.

Adiabatic calorimetry

A precision automatic adiabatic calorimeter was used to measure heat capacities over the temperature range $78 \leq (T/K) \leq 390$. The calorimeter was established in the Thermochemistry Laboratory of the Dalian Institute of Chemical Physics, Chinese Academy of Sciences, China. The principle and structure of the adiabatic calorimeter were described in detail elsewhere [12, 13]. To verify the accuracy of the calorimeter, the heat capacities of the reference standard material (α-Al_2O_3) were measured over the temperature range $78 \leq (T/K) \leq 390$. The sample mass used was 1.7143 g, which was equivalent to 0.0168 mol based on its molar mass, $M(\alpha\text{-}Al_2O_3) = 101.9613$ g mol^{-1}. Deviations of the experimental results from those of the smoothed curve lie within ±0.2%, while the uncertainty is ±0.3%, as compared with the values given by the former National Bureau of Standards [14] over the whole temperature range. Heat capacity measurements were continuously and automatically carried out by means of the standard method of intermittently heating the sample and alternately measuring the temperature. The heating rate and temperature increments were generally controlled at (0.1–0.4) K min^{-1} and (1–3) K. The heating duration was 10 min, and the temperature drift rates of the sample cell measured in an equilibrium period were always kept within (10^{-3} to 10^{-4}) K min^{-1} during the acquisition of all heat capacity data. The data of heat capacities and corresponding equilibrium temperature have been corrected for heat exchange of the sample cell with its surroundings [12, 13].

Results and discussion

Low-temperature heat capacity

The 98 experimental points in the temperature range 78–404 K for $La(Me_2dtc)_3(C_{12}H_8N_2)$, 96 experimental points in the temperature range 78–400 K for $Pr(Me_2dtc)_3(C_{12}H_8N_2)$, 115 experimental points in the temperature range 78–400 K for $Nd(Me_2dtc)_3(C_{12}H_8N_2)$ and 105 experimental points in the temperature range 78–400 K for $Sm(Me_2dtc)_3(C_{12}H_8N_2)$ were fitted by means of the least squares method and the polynomial equations of the experimental molar heat capacities ($C_{p,m}$) versus reduced temperature. (X), $X = f(T)$, have been obtained. All experimental results plotted in Figs. 1, 2, 3, and 4, showed that the structure of the coordination compounds

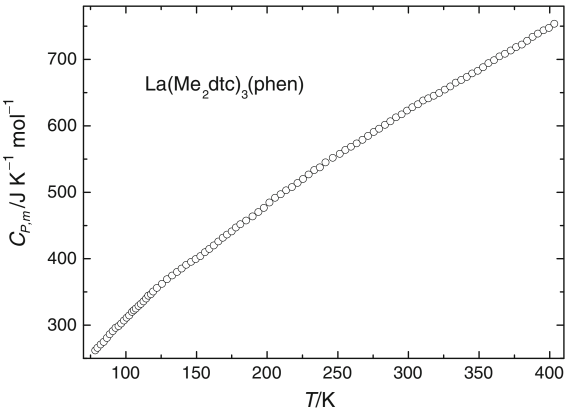

Fig. 1 The curve of experimental molar heat capacities of $La(Me_2dtc)_3(C_{12}H_8N_2)(s)$

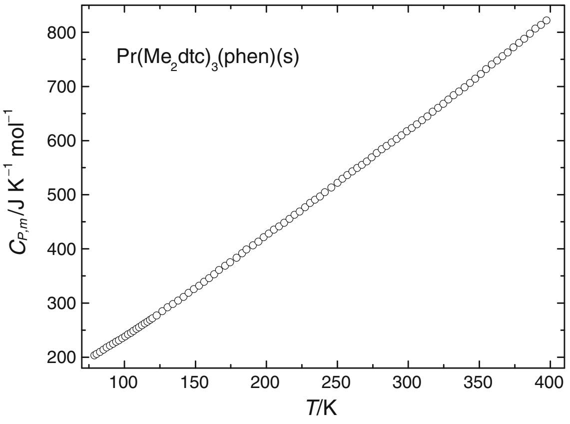

Fig. 2 The curve of experimental molar heat capacities of $Pr(Me_2dtc)_3(C_{12}H_8N_2)(s)$

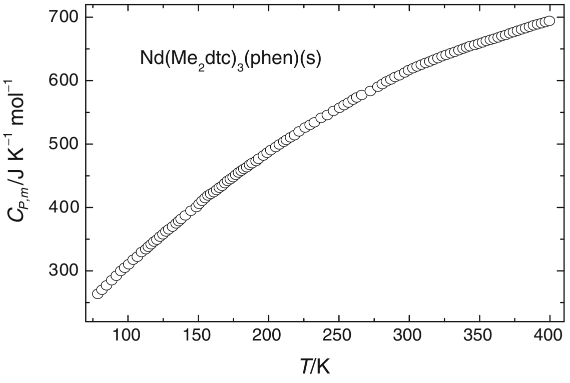

Fig. 3 The curve of experimental molar heat capacities of $Nd(Me_2dtc)_3(C_{12}H_8N_2)(s)$

were stable over the temperature range between $T = 78$ and 404 K, that is, no phase change, association nor thermal decomposition occurred.

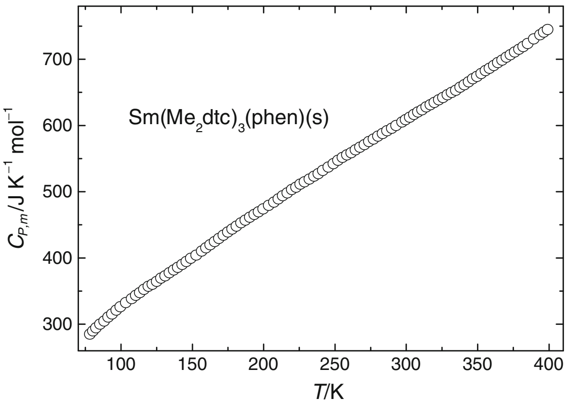

Fig. 4 The curve of experimental molar heat capacities of $Sm(Me_2dtc)_3(C_{12}H_8N_2)(s)$

$$C_{p,m}\left[\mathrm{La(Me_2dtc)_3(C_{12}H_8N_2)}\right] = 542.097 + 229.576X - 27.169X^2 + 14.596X^3 - 7.135X^4 \quad \left(\mathrm{J\ K^{-1}\ mol^{-1}}\right) \tag{1}$$

$$C_{p,m}\left[\mathrm{Pr(Me_2dtc)_3(C_{12}H_8N_2)}\right] = 500.252 + 314.114X - 17.596X^2 - 0.131X^3 + 16.627X^4 \quad \left(\mathrm{J\ K^{-1}\ mol^{-1}}\right) \tag{2}$$

$$C_{p,m}\left[\mathrm{Nd(Me_2dtc)_3(C_{12}H_8N_2)}\right] = 543.586 + 213.876X - 68.040X^2 + 1.173X^3 + 2.563X^4 \quad \left(\mathrm{J\ K^{-1}\ mol^{-1}}\right) \tag{3}$$

$$C_{p,m}\left[\mathrm{Sm(Me_2dtc)_3(C_{12}H_8N_2)}\right] = 528.650 + 216.408X - 16.492X^2 + 12.076X^3 + 4.912X^4 \quad \left(\mathrm{J\ K^{-1}\ mol^{-1}}\right) \tag{4}$$

In (1) $X = (T - 241)/163$. $X = f(T) = [T/\mathrm{K} - 1/2(T_1 + T_2)]/[1/2(T_1 - T_2)]$, where $T_1 = 404$ K and $T_2 = 78$ K. In (2)–(4) $X = (T - 239)/161$. $X = f(T) = [T/\mathrm{K} - 1/2(T_1 + T_2)]/[1/2(T_1 - T_2)]$, where $T_1 = 400$ K and $T_2 = 78$ K. The correlation coefficient for the fitting $R^2 = 0.9998$. The standard deviations of experimental molar heat capacities from the smoothed heat capacities calculated by the polynomial equations were within ±0.3% except for several points around the lower and upper temperature limits.

An attempt is made to estimate the heat capacities of $Ce(Me_2dtc)_3(C_{12}H_8N_2)$ and $Pm(Me_2dtc)_3(C_{12}H_8N_2)$. Figure 5 presents experimental molar heat capacities versus reduced atomic number, from which the polynomial equation of the experimental molar heat capacities versus reduced atomic number is obtained. The reduced atomic number X expression in terms of atomic number n has the form: $X = f(n) = \left[n - \frac{1}{2}(n_1 + n_2)\right] / \left[\frac{1}{2}(n_1 - n_2)\right]$ (where $n_1 = 62$, $n_2 = 57$). The calculated heat capacities of $Ce(Me_2dtc)_3(C_{12}H_8N_2)$ and $Pm(Me_2dtc)_3(C_{12}H_8N_2)$ at 298.15 K are derived to be 617.99 J K^{-1} mol^{-1}, 610.09 J K^{-1} mol^{-1}, respectively (Table 1).

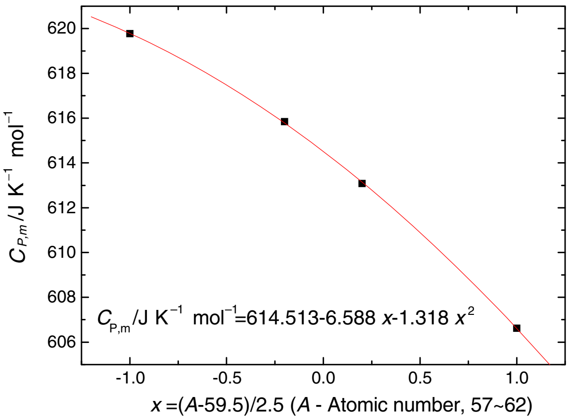

Fig. 5 Curve of the experimental molar heat capacities versus reduced atomic number

Table 1 Data used to evaluate the heat capacities of $Ce(Me_2dtc)_3(C_{12}H_8N_2)$ and $Pm(Me_2dtc)_3(C_{12}H_8N_2)$ at 298.15 K

Atomic numbers, A	Reduced atomic number, x	Calculated heat capacities, $C_{p,m}$/ J K^{-1} mol^{-1}
57	−1	619.78
58	−0.6	617.99
59	−0.2	615.78
60	0.2	613.14
61	0.6	610.09
62	1	606.61

$x = (A - 59.5)/2.5 = \{A - [1/2(A_1 + A_2)]\}/[1/2(A_1 - A_2)]\}$ $(A_1 = 62, A_2 = 57)$

Thermodynamic functions

The smoothed molar heat capacities and thermodynamic functions of $Ln(Me_2dtc)_3(C_{12}H_8N_2)(s)$ were calculated based on the fitted polynomial of the heat capacities as a function of the reduced temperature (X) according to the following thermodynamic equations.

$$(H_T - H_{298.15}) = \int_{298.15}^{T} C_p \mathrm{d}T \qquad (5)$$

$$(S_T - S_{298.15}) = \int_{298.15}^{T} C_p T^{-1} \mathrm{d}T \qquad (6)$$

$$(G_T - G_{298.15}) = \int_{298.15}^{T} C_p \mathrm{d}T - T\int_{298.15}^{T} C_p T^{-1} \mathrm{d}T \qquad (7)$$

The polynomial fitted values of the molar heat capacities and fundamental thermodynamic functions of the sample relative to the standard reference temperature 298.15 K

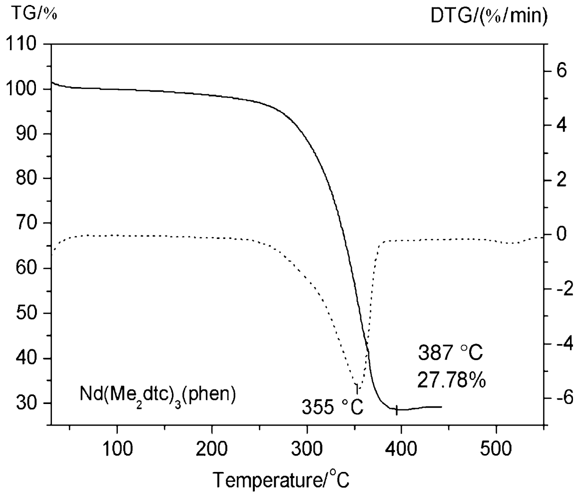

Fig. 6 TG-DTG curves of the complex $Nd(Me_2dtc)_3(C_{12}H_8N_2)$

Table 2 Smoothed heat capacities and thermodynamic functions of $La(Me_2dtc)_3(phen)$

T/K	$C_{p,m}$/ J K^{-1} mol^{-1}	$(H_T - H_{298.15\ K})$/ kJ mol^{-1}	$(S_T - S_{298.15\ K})$/ J K^{-1} mol^{-1}	$(G_T - G_{298.15\ K})$/ kJ mol^{-1}
80	267.97	−146.7	293.9	−225.4
85	278.71	−144.7	280.8	−223.0
90	289.25	−142.6	268.2	−220.2
95	299.59	−140.4	255.9	−217.1
100	309.73	−138.2	244.1	−213.8
105	319.70	−135.9	232.6	−210.3
110	329.49	−133.5	221.5	−206.5
115	339.11	−131.1	210.8	−202.5
120	348.57	−128.5	200.4	−198.4
125	357.87	−126.0	190.4	−194.1
130	367.02	−123.3	180.7	−189.6
135	376.02	−120.6	171.4	−185.0
140	384.89	−117.8	162.4	−180.3
145	393.62	−114.9	153.7	−175.4
150	402.23	−112.0	145.3	−170.5
155	410.71	−109.0	137.2	−165.4
160	419.08	−106.0	129.5	−160.3
165	427.33	−102.9	122.0	−155.0
170	435.48	−99.73	114.8	−149.7
175	443.52	−96.51	107.8	−144.3
180	451.47	−93.23	101.2	−138.9
185	459.33	−89.89	94.76	−133.4
190	467.09	−86.49	88.59	−127.9
195	474.77	−83.04	82.67	−122.3
200	482.37	−79.53	76.97	−116.7
205	489.89	−75.97	71.49	−111.0
210	497.34	−72.35	66.23	−105.3
215	504.72	−68.68	61.18	−99.55

Table 2 continued

T/K	$C_{p,m}$/ J K^{-1} mol^{-1}	$(H_T - H_{298.15\ K})$/ kJ mol^{-1}	$(S_T - S_{298.15\ K})$/ J K^{-1} mol^{-1}	$(G_T - G_{298.15\ K})$/ kJ mol^{-1}
220	512.04	−64.95	56.33	−93.79
225	519.29	−61.17	51.66	−87.99
230	526.48	−57.33	47.18	−82.17
235	533.61	−53.45	42.87	−76.32
240	540.69	−49.51	38.73	−70.45
245	547.71	−45.52	34.74	−64.55
250	554.69	−41.48	30.90	−58.62
255	561.62	−37.39	27.21	−52.67
260	568.51	−33.24	23.65	−46.69
265	575.35	−29.05	20.21	−40.68
270	582.16	−24.81	16.89	−34.64
275	588.92	−20.52	13.68	−28.57
280	595.65	−16.17	10.57	−22.47
285	602.34	−11.78	7.554	−16.33
290	608.99	−7.342	4.621	−10.16
295	615.62	−2.853	1.764	−3.939
298.15	619.77	0	0	0
300	622.20	1.684	−1.024	2.322
305	628.76	6.270	−3.753	8.630
310	635.29	10.90	−6.429	14.99
315	641.78	15.59	−9.062	21.40
320	648.25	20.31	−11.66	27.87
325	654.68	25.09	−14.23	34.41
330	661.09	29.91	−16.78	41.01
335	667.46	34.78	−19.32	47.68
340	673.81	39.70	−21.85	54.43
345	680.12	44.66	−24.39	61.25
350	686.41	49.67	−26.95	68.17
355	692.66	54.73	−29.52	75.18
360	698.87	59.83	−32.13	82.28
365	705.06	64.98	−34.77	89.49
370	711.20	70.17	−37.46	96.81
375	717.32	75.40	−40.20	104.2
380	723.39	80.68	−43.01	111.8
385	729.43	86.01	−45.88	119.5
390	735.42	91.38	−48.83	127.3
395	741.37	96.79	−51.87	135.2
400	747.27	102.3	−55.00	143.4

were tabulated in Tables 2, 3, 4, and 5 with the interval of 5 K.

Thermal decomposition of Nd(Me_2dtc)$_3$($C_{12}H_8N_2$)

TG-DTG curve of the Nd(Me_2dtc)$_3$($C_{12}H_8N_2$) is presented in Fig. 6. The complex is decomposed into the final

Table 3 Smoothed heat capacities and thermodynamic functions of Pr(Me_2dtc)$_3$(phen) ($M = 681.74$ g mol^{-1})

T/K	$C_{p,m}$/ J K^{-1} mol^{-1}	$(H_T - H_{298.15\ K})$/ kJ mol^{-1}	$(S_T - S_{298.15\ K})$/ J K^{-1} mol^{-1}	$(G_T - G_{298.15\ K})$/ kJ mol^{-1}
80	205.17	−88.35	−475.0	−50.34
85	213.07	−87.30	−462.5	−47.99
90	221.14	−86.22	−450.1	−45.71
95	229.37	−85.09	−437.9	−43.49
100	237.76	−83.92	−425.9	−41.34
105	246.29	−82.71	−414.0	−39.24
110	254.96	−81.46	−402.3	−37.21
115	263.74	−80.16	−390.7	−35.23
120	272.64	−78.82	−379.2	−33.31
125	281.64	−77.44	−367.9	−31.45
130	290.74	−76.01	−356.6	−29.65
135	299.93	−74.53	−345.4	−27.89
140	309.19	−73.01	−334.3	−26.20
145	318.53	−71.44	−323.3	−24.55
150	327.93	−69.82	−312.4	−22.96
155	337.39	−68.16	−301.5	−21.43
160	346.90	−66.45	−290.7	−19.94
165	356.46	−64.69	−279.9	−18.51
170	366.05	−62.88	−269.1	−17.13
175	375.68	−61.03	−258.4	−15.81
180	385.34	−59.12	−247.7	−14.53
185	395.02	−57.17	−237.1	−13.31
190	404.72	−55.17	−226.5	−12.15
195	414.44	−53.13	−215.9	−11.04
200	424.17	−51.03	−205.3	−9.976
205	433.91	−48.88	−194.7	−8.970
210	443.66	−46.69	−184.2	−8.018
215	453.42	−44.45	−173.6	−7.119
220	463.17	−42.16	−163.1	−6.275
225	472.93	−39.82	−152.6	−5.484
230	482.69	−37.43	−142.1	−4.746
235	492.45	−34.99	−131.6	−4.063
240	502.20	−32.50	−121.1	−3.433
245	511.96	−29.97	−110.7	−2.857
250	521.71	−27.38	−100.2	−2.335
255	531.46	−24.75	−89.74	−1.866
260	541.21	−22.07	−79.30	−1.450
265	550.97	−19.34	−68.87	−1.087
270	560.73	−16.56	−58.45	−0.7766
275	570.49	−13.73	−48.04	−0.5188
280	580.26	−10.85	−37.65	−0.3131
285	590.04	−7.928	−27.26	−0.1593
290	599.83	−4.954	−16.89	−0.05705
295	609.65	−1.930	−6.522	−0.005995
298.15	615.84	0	0	0
300	619.48	1.143	3.828	−0.005834

Table 3 continued

T/K	$C_{p,m}$/ J K^{-1} mol^{-1}	($H_T -$ $H_{298.15\ \mathrm{K}}$)/ kJ mol^{-1}	($S_T -$ $S_{298.15\ \mathrm{K}}$)/ J K^{-1} mol^{-1}	($G_T -$ $G_{298.15\ \mathrm{K}}$)/ kJ mol^{-1}
305	629.34	4.265	14.17	−0.05626
310	639.23	7.436	24.49	−0.1570
315	649.16	10.66	34.81	−0.3078
320	659.12	13.93	45.11	−0.5083
325	669.14	17.25	55.41	−0.7585
330	679.20	20.62	65.69	−1.058
335	689.33	24.04	75.96	−1.407
340	699.52	27.51	86.23	−1.806
345	709.79	31.04	96.49	−2.254
350	720.13	34.61	106.7	−2.752
355	730.57	38.24	117.0	−3.300
360	741.10	41.92	127.3	−3.898
365	751.75	45.65	137.5	−4.548
370	762.50	49.43	147.8	−5.250
375	773.38	53.27	158.1	−6.005
380	784.40	57.17	168.4	−6.814
385	795.56	61.12	178.7	−7.678
390	806.88	65.12	189.0	−8.600
395	818.37	69.19	199.4	−9.581
400	830.03	73.31	209.8	−10.62

Table 4 Smoothed heat capacities and thermodynamic functions of Nd(Me$_2$dtc)$_3$(phen)(s)

T/K	$C_{p,m}$/ J K^{-1} mol^{-1}	($H_T -$ $H_{298.15\ \mathrm{K}}$)/ kJ mol^{-1}	($S_T - S_{298.15\mathrm{K}}$)/ J K^{-1} mol^{-1}	($G_T -$ $G_{298.15\ \mathrm{K}}$)/ kJ mol^{-1}
80	267.31	−100.5	−555.5	48.03
85	277.88	−99.09	−539.2	50.73
90	288.33	−97.68	−523.1	53.14
95	298.66	−96.21	−507.3	55.29
100	308.89	−94.69	−491.7	57.18
105	319.00	−93.12	−476.3	58.82
110	328.99	−91.50	−461.1	60.21
115	338.87	−89.83	−446.2	61.37
120	348.62	−88.11	−431.5	62.31
125	358.26	−86.34	−416.9	63.03
130	367.78	−84.53	−402.6	63.54
135	377.17	−82.66	−388.4	63.84
140	386.44	−80.75	−374.5	63.95
145	395.58	−78.80	−360.7	63.88
150	404.61	−76.80	−347.0	63.62
155	413.50	−74.75	−333.6	63.18
160	422.27	−72.66	−320.3	62.58
165	430.91	−70.53	−307.1	61.81
170	439.42	−68.36	−294.1	60.89
175	447.81	−66.14	−281.3	59.82
180	456.06	−63.88	−268.6	58.60
185	464.19	−61.58	−256.0	57.24
190	472.18	−59.24	−243.5	55.75
195	480.04	−56.85	−231.2	54.13
200	487.78	−54.44	−219.0	52.39
205	495.38	−51.98	−206.9	50.52
210	502.85	−49.48	−194.9	48.55
215	510.19	−46.95	−183.1	46.46
220	517.40	−44.38	−171.3	44.27
225	524.47	−41.78	−159.7	41.99
230	531.42	−39.14	−148.2	39.60
235	538.23	−36.46	−136.7	37.13
240	544.91	−33.75	−125.4	34.58
245	551.46	−31.01	−114.1	31.94
250	557.88	−28.24	−103.0	29.22
255	564.17	−25.43	−91.94	26.43
260	570.33	−22.60	−80.96	23.58
265	576.36	−19.73	−70.08	20.66
270	582.26	−16.83	−59.28	17.68
275	588.03	−13.91	−48.56	14.65
280	593.67	−10.95	−37.93	11.56
285	599.18	−7.972	−27.37	8.429
290	604.57	−4.962	−16.90	5.255
295	609.83	−1.926	−6.507	2.042
298.15	613.08	0	0	0
300	614.97	1.136	3.807	−1.205
305	619.98	4.223	14.04	−4.482
310	624.87	7.336	24.20	−7.785
315	629.64	10.47	34.28	−11.11
320	634.28	13.63	44.28	−14.45
325	638.80	16.81	54.20	−17.81
330	643.21	20.02	64.04	−21.17
335	647.50	23.25	73.80	−24.54
340	651.67	26.50	83.49	−27.91
345	655.72	29.76	93.09	−31.28
350	659.66	33.05	102.6	−34.63
355	663.49	36.36	112.0	−37.98
360	667.21	39.69	121.4	−41.31
365	670.82	43.03	130.7	−44.62
370	674.32	46.40	139.8	−47.90
375	677.71	49.78	148.9	−51.15
380	681.00	53.17	157.9	−54.37
385	684.19	56.59	166.8	−57.55
390	687.28	60.02	175.6	−60.69
395	690.27	63.46	184.3	−63.78
400	693.16	66.92	192.9	−66.82

Table 5 Smoothed heat capacities and thermodynamic functions of $Sm(Me_2dtc)_3(phen)(s)$

T/K	$C_{p,m}$/ J K^{-1} mol^{-1}	$(H_T - H_{298.15\ K})$/ kJ mol^{-1}	$(S_T - S_{298.15\ K})$/ J K^{-1} mol^{-1}	$(G_T - G_{298.15\ K})$/ kJ mol^{-1}
80	291.89	−99.49	−555.0	62.50
85	300.11	−98.01	−537.4	63.27
90	308.28	−96.49	−520.2	63.89
95	316.40	−94.92	−503.4	64.35
100	324.48	−93.32	−486.9	64.68
105	332.50	−91.68	−470.8	64.87
110	340.48	−90.00	−455.0	64.93
115	348.40	−88.27	−439.5	64.86
120	356.28	−86.51	−424.3	64.67
125	364.10	−84.71	−409.4	64.36
130	371.86	−82.87	−394.8	63.95
135	379.58	−80.99	−380.5	63.42
140	387.24	−79.08	−366.4	62.79
145	394.85	−77.12	−352.5	62.06
150	402.40	−75.13	−338.9	61.23
155	409.90	−73.10	−325.5	60.31
160	417.35	−71.03	−312.3	59.29
165	424.75	−68.92	−299.3	58.19
170	432.09	−66.78	−286.5	56.99
175	439.38	−64.60	−273.8	55.71
180	446.63	−62.39	−261.4	54.35
185	453.82	−60.14	−249.1	52.90
190	460.96	−57.85	−237.0	51.38
195	468.06	−55.53	−225.0	49.77
200	475.11	−53.17	−213.1	48.09
205	482.11	−50.78	−201.4	46.32
210	489.07	−48.35	−189.8	44.49
215	495.99	−45.88	−178.3	42.57
220	502.86	−43.39	−167.0	40.58
225	509.70	−40.86	−155.7	38.52
230	516.50	−38.29	−144.6	36.38
235	523.26	−35.69	−133.5	34.17
240	529.99	−33.06	−122.5	31.89
245	536.69	−30.39	−111.7	29.53
250	543.36	−27.69	−100.8	27.10
255	550.01	−24.96	−90.10	24.60
260	556.63	−22.19	−79.44	22.03
265	563.22	−19.39	−68.84	19.38
270	569.80	−16.56	−58.30	16.66
275	576.36	−13.69	−47.82	13.87
280	582.91	−10.80	−37.40	11.00
285	589.45	−7.864	−27.03	8.067
290	595.98	−4.901	−16.71	5.059
295	602.51	−1.904	−6.444	1.978
298.15	606.62	0	0	0
300	609.03	1.124	3.776	−1.175
305	615.56	4.186	13.95	−4.400
310	622.10	7.280	24.08	−7.698
315	628.65	10.41	34.16	−11.07
320	635.20	13.57	44.20	−14.51
325	641.78	16.76	54.19	−18.02
330	648.38	19.98	64.15	−21.61
335	655.01	23.24	74.05	−25.26
340	661.66	26.53	83.91	−28.99
345	668.35	29.86	93.73	−32.78
350	675.08	33.22	103.5	−36.65
355	681.85	36.61	113.2	−40.59
360	688.67	40.04	122.9	−44.59
365	695.54	43.50	132.5	−48.66
370	702.47	46.99	142.1	−52.80
375	709.47	50.52	151.6	−57.00
380	716.53	54.09	161.0	−61.27
385	723.66	57.69	170.4	−65.60
390	730.87	61.32	179.7	−69.99
395	738.17	65.00	188.9	−74.44
400	745.55	68.71	198.1	−78.95

compounds in one step, which begin at 143 °C and complete at 387 °C, accompanying with the mass loss of 72.22%. The decomposition process is postulated as Eq. 4, where 355 °C is the peak value in DTG curve and 28.07% is the calculated value of the mass residual. The experimental result is in good agreement with the calculated result. XRD pattern of the final product from the thermolysis identifies the product as Nd_2S_3 (JCPDS card No. 36-1267).

$$Nd(Me_2dtc)_3(phen) \xrightarrow{143\,^{\circ}C-355\,^{\circ}C-387\,^{\circ}C} \frac{1}{2}Nd_2S_3 + 3C \tag{8}$$

Conclusions

Carried out in the present work has been an experimental research on the heat capacities of $Ln(Me_2dtc)_3(C_{12}H_8N_2)$ (Ln = La, Pr, Nd, Sm) in the temperature range of 79–404 K by adiabatic calorimetry. The obtained heat capacities makes it possible to predict the heat capacities of other metal Pm, Ce complexes with dimethyldithiocarbamate, phenanthroline ligand for which no experimental data are available. Additionally, the thermodynamic functions were derived from these experimental results.

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References

1. Zhang ZF, Liu WM, Xue QJ. Friction and wear properties of film formed in the immersion test of oil containing the complex of lanthanide diethyldithiocarbamate and phenanthroline. Thin Solid Films. 1998;330:120–4.
2. Zhang ZF, Su CY, Liu WM, Xue QJ, Tan MY. Tribological properties and lubricating mechanisms of the rare earth complex as a grease additive. Wear. 1996;194:80–5.
3. Zhang WG, Zhu CY, Li HY, Hu DG. Applied studies (II) on the complexes of RE with sulphur containing organic ligand potence of the $Et_2NH_2[La(S_2CNEt_2)_4]$ complex preventing from disease and promoving vegetable growth. Rare Earth. 1998;19:46–50.
4. Gmelin L. Gmelin handbook of inorganic chemistry, vol. 67. Berlin: Springer-Verlag; 1984. p. 105.
5. Bessegene VL, Ivanova EN, Kovalevskaya YA, Larionov SV. Synthesis and properties of ZnS-EuS films grown from volatile complex compounds. In: Abstracts of papers, spring meeting of the electrochemical society, Los Angeles, 1996, proceedings, vol. 96. Electrochemical Society; 1996. p. 105.
6. Sengupta SK, Kumar S. Thermal studies on metal dithiocarbamato complexes. A review. Thermochim Acta. 1984;72:349–61.
7. Regulacio MD, Tomson N, Stoll SL. Dithiocarbamate precursors for rare-earth sulfides. Chem Mater. 2005;17(12):3114–21.
8. Mirkovic T, Hines MA, Nair PS, Scholes GD. Single-source precursor route for the synthesis of EuS nanocrystals. Chem Mater. 2005;17(13):3451–6.
9. Xue B, Li XF, Wang JY, Yu SJ, Tan ZC, Sun LX. Heat capacities and thermodynamic properties of trans-(R)-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylic acid. J Therm Anal Calorim. 2008;94:529–34.
10. Qiu SJ, Chu HL, Zhang J, Qi YN, Sun LX, Xu F. Heat capacities and thermodynamic properties of CoPc and CoTMPP. J Therm Anal Calorim. 2008;91:841–8.
11. He J, Chen SP, Gao SL. Synthesis, characterization and thermal decomposition of $Ln(Me_2dtc)_3(phen)$. J Rare Earths. 2007;25:74–7.
12. Tan ZC, Sun GY, Sun Y. An adiabatic low-temperature calorimeter for heat capacity measurement of small samples. J Therm Anal Calorim. 1995;45:59–67.
13. Tan ZC, Liu BP, Yan JB, Sun LX. A fully automated precision adiabatic calorimeter in the temperature range from 80 to 400 K. J Comput Appl Chem. 2003;20:265–8.
14. Ditmars DA, Ishihara S, Chang SS, Bernstein G, West ED. Enthalpy and heat-capacity standard reference material: synthetic sapphire (a-Al_2O_3) from 10 to 2250 K. J Res Natl Bur Stand. 1982;87:159–63.