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Standard enthalpies of formation of solid complexes of RE nitrates with histidine

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Abstract

The combustion energies have been determined for fifteen solid complexes of rare-earth nitrate with histidine.The standard enthalpies of combustion, $\Delta_{c,coor}H^{\theta}$, and standard enthalpies of formation, $\Delta_{f,coor}H^{\theta}$, have been calculated for these complexes. The relationship of $\Delta_{f,coor}H^{\theta}$ with the atomic numbers of the elements in the lanthanide series has been examined. The results show that a certain amount of covalence is present in the chemical bond between the rare-earth cations and histidine. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Histidine; Rare-earth nitrate; Solid complexes; Standard enthalpy of formation

1. Introduction

Rare-earth ions possess some special functions in a biological system; for instance, α-amino acids are the basic units of protein in the human body. In order to explore the metabolism and biological effects of rare-earth ions in a biological system, studies on coordination behaviour of rare-earth salts with amino acids have become a popular domain of bio-inorganic chemistry over the past twenty years. However, studies of rare earth with histidine have rarely been reported. Sudhindra et al. [1] prepared RE(III) complexes $Pr(His)_3Cl_3$ and $Nd(His)_3Cl_3$, and Chen et al. [2] prepared 12 complexes $RE(His)_3(NO_3)_3{\cdot}3H_2O$. Gao et al. recently investigated ternary systems $RE(NO_3)_3$–His–H_2O using the method of phase equilibrium. The results indicated that two series of complexes could be formed in these systems. One series has the general formula $RE(His)(NO_3)_3{\cdot}H_2O$ (see Table 1), the other $RE(His)_3(NO_3)_3{\cdot}2H_2O$ (RE=Sm, Gd, Er). Complexes of rare earth with histidine have not so far been investigated by thermochemical methods.

In this paper, fifteen solid complexes of mole ratio 1 : 1 were synthesized in water. The corresponding combustion energies have been determined, using a rotating bomb calorimeter. The standard enthalpies of combustion, $\Delta_{c,coor}H^{\theta}$, and the standard enthalpies of formation, $\Delta_{f,coor}H^{\theta}$, have been calculated. The relationship of $\Delta_{f,coor}H^{\theta}$ with the atomic numbers of the elements in the lanthanide series has been examined.

2. Experimental

2.1. Preparation and composition of the complexes

Based on phase equilibrium data, fifteen solid complexes of mole ratio 1 : 1 were prepared. The

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Table 1
Analytical results related to the composition of the complexes [a] (in %)

Complexes	RE	His	C	H	N
$La(His)(NO_3)_3{\cdot}H_2O$	27.57(27.89)	31.17(31.15)	14.21(14.47)	2.14(2.23)	16.92(16.87)
$Ce(His)(NO_3)_3{\cdot}H_2O$	28.22(28.06)	32.28(31.07)	14.07(14.43)	2.12(2.22)	16.89(16.83)
$Pr(His)(NO_3)_3{\cdot}H_2O$	27.91(28.18)	30.90(31.03)	14.10(14.41)	2.07(2.22)	16.72(16.80)
$Nd(His)(NO_3)_3{\cdot}H_2O$	28.53(28.65)	30.72(30.82)	14.02(14.32)	2.03(2.20)	16.54(16.69)
$Sm(His)(NO_3)_3{\cdot}H_2O$	29.45(29.51)	30.65(30.45)	13.98(14.14)	2.05(2.18)	16.28(16.49)
$Eu(His)(NO_3)_3{\cdot}H_2O$	29.57(29.73)	30.14(30.36)	13.92(14.10)	1.99(2.17)	16.16(16.44)
$Gd(His)(NO_3)_3{\cdot}H_2O$	30.44(30.45)	29.96(30.04)	14.14(13.95)	2.32(2.15)	16.03(16.27)
$Tb(His)(NO_3)_3{\cdot}H_2O$	30.91(30.67)	30.07(29.95)	14.05(13.91)	2.20(2.14)	16.31(16.22)
$Dy(His)(NO_3)_3{\cdot}H_2O$	31.23(31.15)	29.40(29.74)	13.89(13.81)	2.24(2.13)	16.24(16.11)
$Ho(His)(NO_3)_3{\cdot}H_2O$	31.77(31.47)	29.44(29.60)	13.64(13.75)	2.11(2.12)	16.07(16.03)
$Er(His)(NO_3)_3{\cdot}H_2O$	31.42(31.77)	29.43(29.47)	13.78(13.69)	1.96(2.11)	15.82(15.96)
$Tm(His)(NO_3)_3{\cdot}H_2O$	31.54(31.99)	29.31(29.38)	13.50(13.65)	1.99(2.10)	16.02(15.91)
$Yb(His)(NO_3)_3{\cdot}H_2O$	32.43(32.51)	28.83(29.15)	13.38(13.54)	1.89(2.08)	15.63(15.79)
$Lu(His)(NO_3)_3{\cdot}H_2O$	32.51(32.76)	29.01(29.05)	13.29(13.49)	1.94(2.08)	15.80(15.73)
$Y(His)(NO_3)_3{\cdot}H_2O$	19.82(19.84)	34.25(34.63)	15.96(16.08)	2.53(2.47)	18.84(18.75)

[a] The data in brackets are calculated values.

analytical results are summarized in Table 1. RE^{3+} was determined complexometrically with EDTA. Histidine was analyzed by the formalin method. Before it was titrated, the RE^{3+} was removed by precipitating with $K_2C_2O_4$. Carbon, hydrogen, and nitrogen analyses were carried out on a 1106 type elemental analyzer.

2.2. Apparatus and experimental procedures

The precision rotating bomb calorimeter (RBC type 1) and the basic experimental procedures used in this investigation have already been described [3]. The initial temperature was (25.0000±0.0005)°C, and the initial oxygen pressure 2533.125 kPa. The procedures for analyzing the final products of the bomb were the same as in Ref. [4]. Analytical data of the final products show that the combustion reaction is complete without carbon deposits or carbon monoxide formed in the combustion reaction. The final products were shown to be RE_2O_3 or CeO_2 by IR spectroscopy and chemical analysis. The calorimeter RBC type 1 was calibrated with benzoic acid of 99.999 mol% purity. Benzoic acid has an isothermal heat of combustion at 25°C of (-26476.0 ± 5.8)J g^{-1}. The calibrated experimental results with an uncertainty 0.16% are summarized in Table 2.

Table 2
Calibrated experimental results for the energy equivalent of the calorimeter using benzoic acid

No.	Mass of benzoic acid, a/g	Calibrated, ΔT/K	Calibrated heat of acid containing nitrogen, q_N/J	Calibrated heat of combustion wire, q_c/J	Energy eqivalent of calorimeter [a] $-W/(k\ J\ K^{-1})$
1	1.02220	1.5010	17.38	8.55	18.0459
2	1.14830	1.7023	16.83	5.31	17.8708
3	1.06805	1.5870	19.82	7.65	17.8208
4	1.10430	1.6226	33.67	10.80	18.0227
5	0.90470	1.3278	21.72	9.50	18.0513
6	1.04065	1.5352	20.09	7.70	17.9507
7	0.93050	1.3791	25.52	8.10	17.9831
8	0.98310	1.4571	19.82	5.00	17.8665
9	1.08140	1.5978	22.53	9.45	17.9213

[a] $W=17.9359\pm0.0288$ k J K^{-1}.

The energy equivalent of the RBC type 1 calorimeter was calculated according to the following equation

$$W = \frac{Qa + Gb + 5.983c}{\Delta T} \quad (1)$$

where W is the energy equivalent of the RBC type 1 calorimeter (in J K^{-1}), Q the combustion enthalpy of benzoic acid (in J g^{-1}), a the mass of benzoic acid (in g), G the combustion enthalpy of Ni–Cr wire for ignition (0.9 J cm^{-1}), b the length of actual Ni–Cr wire consumed (in cm), 5.983 the formation enthalpy and solution enthalpy of nitric acid corresponding to 1 cm^{-3} of 0.1000 mol dm^{-3} solution of NaOH (in J cm^{-3}), c the volume (in cm^3) of consumed 0.1000 mol dm^{-3} solution of NaOH and T the correct value of the temperature rise.

The correct value of the exchange was calculated by the following equation [5]

$$\Delta(\Delta T) = nV_0 + \frac{V_n - V_0}{\overline{T}_n - \overline{T}_0} \times \left(\frac{T_0 + T_n}{2} + \sum_{i=1}^{n-1} Ti - n\overline{T}_0 \right) \quad (2)$$

where $\Delta(\Delta T)$ denotes the correct value of the heat exchange, n the number of readings for the main (or reaction) period, V_0 and V_n the rates of temperature change at the initial and final stages, respectively, (V is positive when temperature decreases), $\overline{T}_0$, $\overline{T}_n$ the average temperatures of the calorimeter at the initial and final stages, respectively (average temperature for first and last reading), T_0 the last reading of the initial stage, T_n the first reading of the final stage, $\sum_{i=1}^{n-1} T_i$ the sum of all the readings except the last one of the main period, $(V_n - V_0)/(\overline{T}_n - \overline{T}_0)$ must be constant.

3. Results and discussion

3.1. Combustion energy of the samples

The method of combustion energy determination for the samples is the same as that for the calibration of the calorimeter with benzoic acid. The sample masses were determined in vacuum. The combustion energies of the samples were calculated by the following formula

$$\Delta_{c,coor}E = \frac{W\Delta T - Gb - 5.983c}{m} \quad (3)$$

where $\Delta_{c,coor}E$ denotes the constant-volume combustion energy of the sample, and m the mass (in g) of the sample. The other symbols are the same as in Eq. (1). The results of calculations are given in Table 3.

3.2. Standard combustion enthalpies of the complexes

The standard combustion enthalpy of the complexes, $\Delta_{c,coor}H^{\theta}$, refers to the combustion enthalpy change of the following ideal combustion reaction at 298.15 K and 101.325 kPa:

$$RE(His)(NO_3)_3 \cdot H_2O(s) + \frac{7}{2}O_2(g) \rightarrow \frac{1}{2}RE_2O_3(s) + 6CO_2(g) + \frac{11}{2}H_2O(l) + 3N_2(g) \quad (4)$$

$$Ce(His)(NO_3)_3 \cdot H_2O(s) + \frac{15}{4}O_2(g) \rightarrow CeO_2(s) + 6CO_2(g) + \frac{11}{2}H_2O(l) + 3N_2(g) \quad (5)$$

The standard combustion enthalpies of the foregoing complexes were calculated from the combustion energy using the following equations

$$\Delta_{c,coor(s)}H^{\theta} = \Delta_{c,coor(s)}E + \Delta nRT \quad (6)$$

$$\Delta n = n_{gas}(\text{products}) - n_{gas}(\text{reactants})$$

where n_{gas} is the total amount (in mol) of gas present as products or reactants and T=298.15 K. The results of the calculations are given in Table 4.

3.3. Standard enthalpies of formation of the complexes

The standard enthalpies of formation of the above complexes were calculated by Hess' law according to the following thermochemical equation:

$$\Delta_{f,coor(s)}H^{\theta} = \frac{1}{2}\Delta_{f,Re_2O_3(s)}H^{\theta} + 6\Delta_{f,CO_2(g)}H^{\theta} + \frac{11}{2}\Delta_{f,H_2O(l)}H^{\theta} - \Delta_{c,coor(s)}H^{\theta} \quad (7)$$

Table 3
Combustion energy of the complexes

Complex	No.	Mass of complex, m/g	Calibrated heat of combustion wire, q_c/J	Calibrated heat of acid containing nitrogen, q_N/J	Calibrated heat of plastic film q_f/J	Calibrated ΔT/K	Combustion energy, $-\Delta E$/J g^{-1}
La(His)$(NO_3)_3\cdot H_2O$	1	1.03260	12.66	22.80	794.52	0.3742	5696.49
	2	1.10485	11.78	25.04	789.93	0.3973	5700.84
	3	0.98727	10.80	22.06	750.27	0.3563	5680.62
	4	0.96730	12.60	2.00	800.54	0.3531	5684.37
	5	1.05468	12.60	23.26	803.83	0.3778	5723.45
	6	1.00690	11.76	22.25	698.65	0.3612	5707.23
	average						5698.83±5.84
Ce(His)$(NO_3)_3\cdot H_2O$	1	1.29760	11.70	26.83	372.43	0.3961	5158.79
	2	1.20545	12.60	25.02	409.21	0.3709	5147.23
	3	1.00367	10.87	24.06	384.58	0.3127	5169.36
	4	1.03258	11.78	24.47	385.57	0.3201	5150.81
	5	0.99864	12.60	24.00	390.62	0.3105	5148.47
	6	1.00427	10.86	24.09	403.37	0.3124	5143.28
	average						5152.99±3.55
Pr(His)$(NO_3)_3\cdot H_2O$	1	1.03579	11.28	26.00	647.30	0.3518	5430.49
	2	1.00065	11.65	24.98	684.57	0.3425	5417.93
	3	1.00346	12.60	25.06	632.46	0.3416	5438.27
	4	0.98977	11.70	24.27	673.58	0.3387	5420.85
	5	0.99943	10.88	24.83	654.62	0.3417	5442.13
	6	1.05327	10.62	26.24	637.39	0.3565	5430.66
	average						5430.00±3.52
Nd(His)$(NO_3)_3\cdot H_2O$	1	1.17795	10.65	24.59	758.65	0.3867	5213.78
	2	1.06630	11.68	20.20	611.98	0.3454	5206.43
	3	1.00273	13.06	18.95	764.72	0.3349	5195.74
	4	0.99862	11.70	18.06	733.56	0.3320	5198.85
	5	1.00035	12.60	19.00	747.89	0.3349	5225.20
	6	1.03257	12.60	20.01	728.45	0.3431	5222.12
	average						5210.35±4.51
Sm(His)$(NO_3)_3\cdot H_2O$	1	1.02485	11.08	21.96	487.84	0.3492	5604.26
	2	0.98963	12.60	20.03	551.29	0.3447	5656.28
	3	0.94830	12.60	19.89	486.05	0.3266	5629.84
	4	1.03570	11.78	22.04	467.77	0.3535	5637.59
	5	1.00362	10.68	21.08	496.26	0.3454	5647.43
	6	1.05786	11.76	22.45	500.43	0.3623	5638.25
	average						5635.69±6.70
Eu(His)$(NO_3)_3\cdot H_2O$	1	1.00354	11.68	25.06	819.35	0.3393	5210.48
	2	1.06238	11.70	26.48	745.23	0.3515	5196.79
	3	0.98723	12.60	24.96	789.36	0.3318	5189.65
	4	0.99060	10.08	25.00	697.47	0.3270	5180.46
	5	1.03072	12.60	25.98	800.35	0.3446	5182.32
	6	1.00467	9.80	25.12	790.59	0.3364	5184.10
	average						5190.63±4.24
Gd(His)$(NO_3)_3\cdot H_2O$	1	1.02453	11.70	25.42	866.70	0.3057	4470.03
	2	0.98620	12.68	25.00	845.37	0.2949	4468.24

Table 3 (*Continued*)

Complex	No.	Mass of complex, m/g	Calibrated heat of combustion wire, q_c/J	Calibrated heat of acid containing nitrogen, q_N/J	Calibrated heat of plastic film q_f/J	Calibrated ΔT/K	Combustion energy, $-\Delta E$/J g^{-1}
	3	0.96375	10/80	24.96	804.32	0.2868	4465.47
	4	1.00046	11.70	25.22	813.06	0.2962	4460.98
	5	0.94532	9.98	24.58	798.43	0.2814	4458.62
	6	0.99001	12.60	25.06	767.58	0.2925	4485.81
	average						4468.19±3.59
$Tb(His)(NO_3)_3{\cdot}H_2O$	1	1.00650	12.60	26.02	834.27	0.3360	5120.32
	2	1.10375	13.05	28.00	847.35	0.3655	5135.10
	3	1.00038	12.60	25.67	833.42	0.3331	5100.45
	4	1.00492	11.70	25.90	845.33	0.3349	5098.65
	5	0.99970	10.68	25.06	827.00	0.3338	5125.43
	6	0.98935	11.70	24.52	831.47	0.3304	5113.46
	average						5115.57±5.32
$Dy(His)(NO_3)_3{\cdot}H_2O$	1	1.17805	13.05	21.96	829.92	0.4007	5367.07
	2	1.01960	12.60	20.00	400.02	0.3304	5387.54
	3	1.02050	11.70	19.52	673.27	0.3433	5342.60
	4	1.00021	11.70	19.07	834.53	0.3460	5339.95
	5	1.00345	12.60	19.23	786.42	0.3472	5389.67
	6	0.99727	11.68	19.00	785.34	0.3450	5386.46
	average						5368.88±8.53
$Ho(His)(NO_3)_3{\cdot}H_2O$	1	1.06840	13.05	24.02	458.43	0.3612	5600.34
	2	1.00045	12.60	23.00	563.54	0.3483	5644.78
	3	1.00325	13.05	23.53	574.69	0.3479	5610.59
	4	0.99824	11.70	23.00	594.35	0.3492	5643.26
	5	0.99765	12.60	22.85	564.58	0.3469	5635.14
	6	1.10076	10.86	24.57	523.46	0.3755	5611.03
	average						5624.19±7.14
$Er(His)(NO_3)_3{\cdot}H_2O$	1	0.97210	11.70	24.59	561.40	0.3116	5134.23
	2	1.00265	12.60	25.87	771.07	0.3351	5187.16
	3	1.00046	12.60	25.54	723.25	0.3320	5190.23
	4	0.99835	12.60	25.00	731.40	0.3302	5162.47
	5	1.01250	11.70	26.07	656.57	0.3309	5175.45
	6	0.92357	10.86	24.23	674.86	0.3058	5170.06
	average						5169.93±7.58
$Tm(His)(NO_3)_3{\cdot}H_2O$	1	0.96215	11.70	20.59	659.80	0.3157	5166.01
	2	1.06327	11.68	22.73	592.38	0.3385	5119.78
	3	1.00438	10.80	21.00	646.72	0.3248	5124.35
	4	1.00523	12.66	21.08	654.60	0.3253	5120.23
	5	1.03146	12.60	22.00	637.54	0.3319	5120.37
	6	0.97238	12.60	21.04	627.36	0.3135	5103.10
	average						5125.64±7.87
$Yb(His)(NO_3)_3{\cdot}H_2O$	1	1.11850	12.60	23.71	685.09	0.3593	5116.64
	2	1.16435	12.60	24.34	537.95	0.3662	5147.50
	3	1.00724	11.70	21.65	585.43	0.3228	5134.01
	4	1.00030	12.60	21.00	594.27	0.3231	5165.06
	5	0.98267	12.60	20.52	610.13	0.3158	5109.97
	6	0.97458	11.70	20.01	620.32	0.3150	5128.03

Table 3 (*Continued*)

Complex	No.	Mass of complex, m/g	Calibrated heat of combustion wire, q_c/J	Calibrated heat of acid containing nitrogen, q_N/J	Calibrated heat of plastic film q_f/J	Calibrated ΔT/K	Combustion energy, $-\Delta E$/J g^{-1}
	average						5133.54±7.56
$Lu(His)(NO_3)_3 \cdot H_2O$	1	1.00040	12.60	24.02	394.04	0.3467	5786.25
	2	1.00652	12.60	24.56	454.62	0.3529	5800.07
	3	1.00034	11.70	24.50	351.78	0.3452	5801.23
	4	0.86475	12.60	21.47	395.27	0.3019	5765.35
	5	0.85480	11.70	21.00	456.36	0.3022	5768.78
	6	0.96753	12.60	22.54	457.20	0.3401	5796.06
	average						5786.29±5.90
$Y(His)(NO_3)_3 \cdot H_2O$	1	0.97955	11.70	21.84	678.19	0.6236	8732.11
	2	0.68925	12.60	15.60	648.30	0.4483	8739.32
	3	0.99278	11.53	22.12	685.27	0.6317	8718.90
	4	1.00030	10.80	23.00	683.45	0.6369	8724.35
	5	1.00246	9.98	23.14	676.38	0.6360	8714.97
	6	1.01374	12.60	24.60	684.26	0.6452	8727.49
	average						8726.19±4.48

Table 4
Combustion energy, standard enthalpy of combustion and standard enthalpy of the formation of the complexes $RE(His)(NO_3)_3{\cdot}H_2O$

Complexes	Number of experiments	$-\Delta_{c,coor}E$/kJ mol^{-1}	$-\Delta_{c,coor}H^{\theta}$/kJ mol^{-1}	$-\Delta_{f,coor}H^{\theta}$/kJ mol^{-1}
$La(His)(NO_3)_3{\cdot}H_2O$	6	2838.02±2.91	2824.39±2.91	2005.30±3.12
$Ce(His)(NO_3)_3{\cdot}H_2O$	6	2572.89±1.77	2559.88±1.77	2461.83±2.39
$Pr(His)(NO_3)_3{\cdot}H_2O$	6	2715.49±1.76	2701.86±1.76	2145.06±2.46
$Nd(His)(NO_3)_3{\cdot}H_2O$	6	2623.00±2.27	2609.37±2.27	2227.81±2.61
$Pm(His)(NO_3)_3{\cdot}H_2O$	—			2150 [a]
$Sm(His)(NO_3)_3{\cdot}H_2O$	6	2871.55±3.41	2857.92±3.41	1982.90±4.04
$Eu(His)(NO_3)_3{\cdot}H_2O$	6	2652.41±2.17	2638.78±2.17	2125.84±2.83
$Gd(His)(NO_3)_3{\cdot}H_2O$	6	2307.51±1.85	2293.88±1.85	2547.04±4.13
$Tb(His)(NO_3)_3{\cdot}H_2O$	5	2650.43±2.76	2636.80±2.76	2210.12±3.23
$Dy(His)(NO_3)_3{\cdot}H_2O$	6	2800.84±4.45	2786.37±4.45	2079.35±5.97
$Ho(His)(NO_3)_3{\cdot}H_2O$	5	2947.69±3.74	2934.06±3.74	1939.63±6.31
$Er(His)(NO_3)_3{\cdot}H_2O$	6	2721.66±3.99	2708.03±3.99	2165.00±4.48
$Tm(His)(NO_3)_3{\cdot}H_2O$	5	2706.95±4.16	2693.32±4.16	2184.13±7.32
$Yb(His)(NO_3)_3{\cdot}H_2O$	6	2732.17±4.02	2718.54±4.02	2121.84±4.66
$Lu(His)(NO_3)_3{\cdot}H_2O$	4	3090.75±3.15	3077.12±3.15	1803.25±8.20
$Y(His)(NO_3)_3{\cdot}H_2O$	6	3910.12±2.01	3896.49±2.01	1942.24±3.13

[a] Estimated value.

$$\Delta_{f,Ce(His)(NO_3)_3\cdot H_2O(s)}H^{\theta} = \Delta_{f,CeO_2(s)}H^{\theta} + 6\Delta_{f,CO_2(g)}H^{\theta} + \frac{11}{2}\Delta_{f,H_2O(l)}H^{\theta} - \Delta_{c,Ce(His)(NO_3)_3\cdot H_2O(s)}H^{\theta} \quad (8)$$

In Eqs. (7) and (8), $\{\Delta_{f,RE_2O_3(s)}\}$ H^{θ} (in kJ mol^{-1})= −1793.14±0.79 (La), −1827.60 (Pr), −1808.12±1.00 (Nd), −1815.40±2.01 (Sm), −1663.00 (Eu), −1815.60 ±3.60 (Gd), −1827.60 (Tb), −1865.39± 3.89 (Dy), −1881.13±5.02 (Ho), −1897.82±1.88 (Er), −1888.66 ±5.86 (Tm), −1814.5±2.22 (Yb), −1881.96±7.53 (Lu) and −1905.60±2.26 (Y) [6]; $\Delta_{f,CeO_2(s)}H^{\theta}$= (-1088.59±1.38) kJ mol^{-1} [7]; $\Delta_{f,CO_2(g)}H^{\theta}$ =(-393.51 ±0.13) kJ mol^{-1} [7]; $\Delta_{f,H_2O(l)}H^{\theta}$=(-285.83±0.042) kJ mol^{-1} [7].

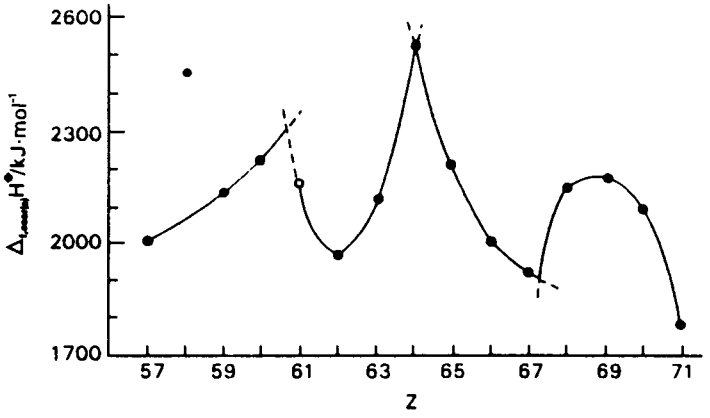

Fig. 1. Plot of $\Delta_{f,coor}H^{\theta}$ values against the atomic number of the lanthanoids.

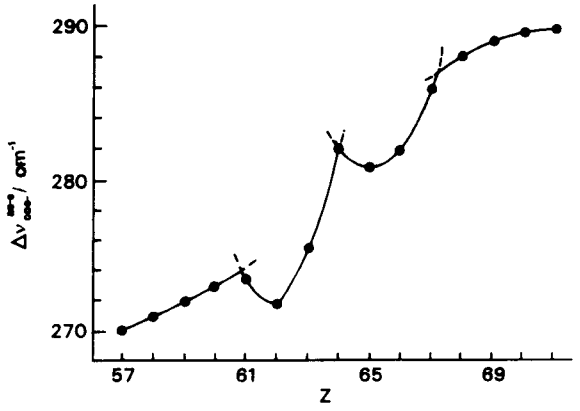

Fig. 2. Plot of $\Delta\nu_{coo^-}^{as-s}$ against the atomic number of lanthanoids for the complexes ($\Delta\nu_{coo^-}^{as-s}$ is the difference between $\nu_{coo^-}^{as}$ and $\nu_{coo^-}^{s}$ in IR spectra for the complexes).

The results of the calculations are also given in Table 4.

In Fig. 1, $\Delta_{f,coor}H^{\theta}$ values of the above complexes are plotted against the atomic numbers of the elements in the lanthanide series. It is seen from Fig. 1 that the curve shows the so-called 'tetrad effect'. The observed 'tetrad effect' is consistent with the observed result in IR spectra (Fig. 2). The results show that a certain amount of covalence is present in the chemical bond between the rare-earth cations and His.

The point corresponding to complex Ce(His)$(NO_3)_3{\cdot}H_2O$ is a considerable deviation from the curve because of its final product being CeO_2 when Ce(His)$(NO_3)_3{\cdot}H_2O$ was combusted. Furthermore, corresponding $\Delta_{f,coor(s)}H^{\theta}$ of complex Pm(His)$(NO_3)_3{\cdot}H_2O$ was estimated by interpolation according to the above curve.

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