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Preparation and characterisation of ammonium lanthanide double sulphate monohydrates

P.N. Iyer and P.R. Natarajan

Radiochemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay 400 085 (India)

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Abstract

The ammonium lanthanide double sulphate monohydrates $NH_4Ln(SO_4)_2 \cdot H_2O$ (Ln = Eu–Yb and Y) were synthesised and characterised by chemical, thermal, infrared and X-ray powder diffraction methods. The heats of dehydration were calculated from measurements of the peak areas under the differential thermal analysis curve recorded during thermal dehydration of the compounds. The infrared spectra coupled with X-ray data showed that these compounds are structurally isomorphous to $RbLn(SO_4)_2 \cdot H_2O$ reported in the literature, and that the lanthanide metal ion is coordinated to eight oxygen atoms.

INTRODUCTION

The lanthanides form a number of hydrated double sulphates with alkali metal and ammonium ions. Among the double sulphates formed with ammonium, the tetrahydrates $NH_4Ln(SO_4)_2 \cdot 4H_2O$ are formed by La–Er and Y [1] and are structurally isomorphous with $NH_4Sm(SO_4)_2 \cdot 4H_2O$, as established by X-ray structural analysis [2]. The heavier lanthanides Er–Lu and Y form a dihydrate $NH_4Ln(SO_4)_2 \cdot 2H_2O$, which is structurally isomorphous with $KLu(SO_4)_2 \cdot 2H_2O$ [3, 4]. As a part of systematic studies on the hydrated double sulphates of ammonium ion with lanthanides, the present paper deals with the synthesis and characterisation, by chemical, thermal, IR and X-ray powder diffraction methods, of the compounds of the type $NH_4Ln(SO_4)_2 \cdot H_2O$ (Ln = Eu–Yb and Y).

EXPERIMENTAL

About 3 g of the appropriate lanthanide sulphate octahydrate, prepared from lanthanide oxide of 99.99% purity, was dissolved in 1 M H_2SO_4,

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Correspondence to: P.R. Natarajan, Radiochemistry Division, Bhabha Atomic Energy Research Centre, Trombay, Bombay 400 085, India.

mixed with a 5–10 fold excess of A.R. $(NH_4)_2SO_4$ and evaporated at 85 ± 5°C for crystallisation of the compound. The finely crystalline compounds thus obtained were filtered off using a medium porosity filter funnel, washed with water, alcohol and ether and dried in air. About 1–1.5 g of the compound was obtained during each preparation. However, the monohydrates of La–Sm and Lu could not be obtained under the above conditions. The compounds were chemically analysed; sulphate gravimetrically as $BaSO_4$, lanthanide metal by hydroxide precipitation and ignition to oxide [5], and water of crystallisation from the weight loss recorded during thermal dehydration. The nitrogen content of a typical compound, $NH_4Er(SO_4)_2 \cdot H_2O$, was determined by the Kjeldahl distillation method; the value of 3.50 ± 0.1% showed satisfactory agreement with the expected value of 3.54%. The percentage of nitrogen in all the other compounds was calculated from the weight loss due to $(NH_4)_2SO_4$ on thermal decomposition.

Thermal analysis (TG, thermogravimetry and DTA, differential thermal analysis) was carried out using a model TGD-7000 RH thermobalance in an air flow of 100 ml min^{-1}. Platinum crucibles of 0.5 ml volume were used as containers and preheated alumina was used as reference material

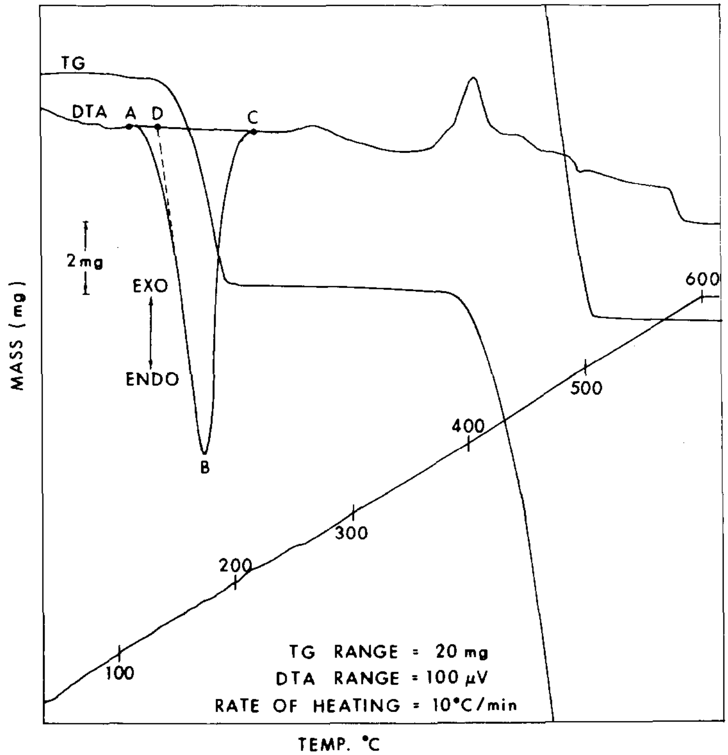

Fig. 1. DTA and TG curves of $NH_4Eu(SO_4)_2 \cdot H_2O$.

for DTA measurements. The area under the DTA peak (ABC in Fig. 1) was obtained by a graphical method. The sum of the number of squares of area 0.05 cm^2 was taken with appropriate weight being given for each fractional division. The area was then converted into heat of dehydration through the calibration constant for the heat of fusion of $KClO_4$. The instrumental parameters were kept identical for all DTA experiments.

A model PU 9500 infrared spectrophotometer was used to record the spectra with the sample dispersed in a Nujol or hexachlorobutadiene mull. The X-ray powder difraction patterns of all the compounds were recorded with a Siemens diffractometer using nickel filterd Cu Kα radiation (λ = 1.54178 Å). Density measurements were made pycknometrically using xylene as displacement fluid.

RESULTS AND DISCUSSION

The analytical results for a few typical $NH_4Ln(SO_4)_2 \cdot H_2O$ compounds are given in Table 1. They are in agreement with the values calculated for the above composition. The thermal dehydrations of all $NH_4Ln(SO_4)_2 \cdot H_2O$ compounds are expressed as

$$NH_4Ln(SO_4)_2 \cdot H_2O \rightarrow NH_4Ln(SO_4)_2 + H_2O \quad (1)$$

The decomposition reactions could be expressed as

$$2NH_4Ln(SO_4)_2 \rightarrow Ln_2(SO_4)_3 + (NH_4)_2SO_4 \quad (2)$$

The TG and DTA curves obtained for the typical compound $NH_4Eu(SO_4)_2 \cdot H_2O$ are shown in Fig. 1. The TG trace was used to check the stoichiometry of water of crystallisation and nitrogen percentage of the compounds. The DTA trace was used to calculate the heat of dehydration of all the $NH_4Ln(SO_4)_2 \cdot H_2O$ compounds. The dehydration temperature was taken as the point at which the baseline intersects with the maximum slope of the DTA peak (point D in Fig. 1). The calibration constant for the instrument was obtained from the measured peak area

TABLE 1

Analytical results for some typical $NH_4Ln(SO_4)_2 \cdot H_2O$ compounds

Metal	Nitrogen (%, TG)		Metal (%)		Sulphate (%)		H_2O (%, TG)	
	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.
Eu	3.68 ± 0.01	3.68	40.4 ± 0.5	40.00	49.5 ± 1.0	50.53	4.7 ± 0.1	4.73
Dy	3.59 ± 0.01	3.59	41.8 ± 0.5	41.61	48.6 ± 1.0	49.17	4.65 ± 0.05	4.61
Tm	3.52 ± 0.01	3.53	42.9 ± 0.5	42.57	48.0 ± 1.0	48.36	4.60 ± 0.1	4.53
Y	4.42 ± 0.01	4.42	28.7 ± 0.5	28.08	59.5 ± 1.0	60.57	5.70 ± 0.1	5.70

TABLE 2

DTA temperature range, temperature of dehydration and heat of dehydration for $NH_4Ln(SO_4)_2 \cdot H_2O$

Element	Temperature range of DTA (°C)	Temperature of dehydration (°C)	Heat of dehydration (kJ mol^{-1})
Eu	130–265	160	64.7 ± 1.2
Gd	120–260	160	66.1 ± 1.3
Tb	115–260	158	67.2 ± 1.2
Dy	120–260	160	67.7 ± 1.0
Ho	120–260	160	68.3 ± 1.3
Er	120–265	156	68.9 ± 1.2
Tm	120–275	160	69.2 ± 1.4
Yb	125–285	170	70.6 ± 1.4
Y	115–265	156	68.2 ± 1.2

recorded during the fusion of $KClO_4$ and using the value of 103.47 ± 1.26 J g^{-1} for its heat of fusion [6]. This calibration constant was used to calculate the heat of dehydration of $CaC_2O_4 \cdot H_2O$ from the DTA peak area recorded during its thermal dehydration. The value of 66.5 ± 0.7 kJ mol^{-1} thus obtained showed satisfactory agreement with the values of 63.64 ± 0.17 kJ mol^{-1} obtained by DSC and 69.45 ± 3.77 kJ mol^{-1} by tensimetry reported in the literature [7]. The heats of dehydration of $NH_4Ln(SO_4)_2 \cdot H_2O$ compounds were calculated from the respective DTA peaks areas, and the averages of three such measurements are given in Table 2. Although the difference in heat of dehydration between two adjacent lanthanides is less than the precision of three measurements, the

TABLE 3

Infrared absorption frequencies in the 4000–400 cm^{-1} range for $NH_4Y(SO_4)_2 \cdot H_2O$

Assignment	Observed frequencies	Assignment	Observed frequencies
$\nu(H_2O)$	3450m,b	$\nu_1(SO_4)$	1010w
$\nu_3(NH_4)$	3260m,b	$\nu_4(SO_4)$	670vs
			640s
$\nu_2 + \nu_6(NH_4)$	2020w,b		605s,b
$\nu_4(NH_4)$	1440s,b	$\nu_2(SO_4)$ + Y–$(OH)_2$wag	485vs
$\delta(H_2O)$	1635vs	Y–OH_2 stretch	430s
$\nu_3(SO_4)$	1190m,b		
	1100m,s		
	1030w,s		

Key: vs, very sharp; s, sharp; m, medium; w, weak; b, broad.

values show an increasing trend with decrease in ionic radius. This could be attributed to the stronger interaction between the oxygen of the coordinated water molecule and the metal ion with decrease in ionic size [8].

The IR spectra showed absorption maxima in the same region for all the compounds, indicating their structural similarity. The observed maxima for the absorption frequencies in the case of a typical compound, $NH_4Y(SO_4)_2 \cdot H_2O$, are listed in Table 3, where they are correlated with the fundamental vibrational modes of various groups. The presence of water of crystallisation in the structure is confirmed by the absorption bands around 3500 cm^{-1} for the O–H stretch and the sharp band at 1635 cm^{-1} for the H–O–H bend.

The water molecule could be present as lattice water or coordinated water [9]. The presence of $Y-OH_2$ stretching and $Y-OH_2$ wagging suggests that the water molecule is coordinated to the metal ion, although the latter feature is mixed with the ν_2 vibrations of the sulphate. The high symmetry, T_d, of the sulphate group is lowered to C_{3v} if unidentate or C_{2v}, if bidentate or bridged. The observed absorption bands at 1190–1030 cm^{-1} show that a bridging bidentate sulphate group exist in the structure, and the absence of the combination ν_4 and ν_6 band for the ammonium ion indicates its possible free rotation in the structure [10]. The assignment of the low frequency bands of the sulphate group is consistent with that reported for lanthanide sulphate hydrates [11].

The structural similarity indicated by the infrared spectra of $NH_4Ln(SO_4)_2 \cdot H_2O$ was confirmed by the X-ray powder diffraction pattern of these compounds. The low angle lines in the powder diffraction patterns of all the compounds could be indexed on a hexagonal unit cell. However, in certain patterns, the strong reflection occurring around $2\theta = 28.5°$ was found to be a doublet. A better fit of the powder data could be obtained when indexed on a monoclinic unit cell with $a \approx c$ and β very close to 120°. The monoclinic symmetry could account for the doublet which was indexed as originating from two independent reflecting planes. This was confirmed by the satisfactory agreement with the measured and calculated densities of the compounds. The indexed powder data for the typical $NH_4Er(SO_4)_2 \cdot H_2O$ are given in Table 4. The space group was deduced to be $P2_1/c$ from the systematically absent reflections; *hol* with *l* odd and *oko* with *k* odd. The crystal data for all the compounds are summarised in Table 5. This indicates that the compounds are isomorphous to $RbLn(SO_4)_2 \cdot H_2O$ in which the rubidium and lanthanide metal ions are in eight-fold coordination. The eight coordination of the lanthanide ion is satisfied by two crystallographically independent tetrahedral sulphate groups (one tetradentate, the other tridentate and both of bridging type) and the oxygen of the water molecule [12]. From the IR evidence indicating coordination of the water oxygen to the metal ion and

TABLE 4

X-ray powder data for $NH_4Er(SO_4)_2 \cdot 4H_2O$. Space group $P2_1/c$

hkl	d_{obs} (Å)	d_{cal} (Å)	I/I_0
$11\bar{1}$	6.765	6.739	100
002	4.982	4.977	11
200	4.923	4.917	12
111	4.846	4.856	4
020	4.617	4.610	12
210 $21\bar{2}$	4.347	4.337 4.348	9
$12\bar{1}$	4.183	4.175	18
102	3.747	3.749	15
121	3.584	3.586	62
112	3.473	3.471	65
$31\bar{1}$	3.438	3.438	40
022	3.373	3.378	2
310	3.088	3.084	8
$13\bar{1}$	2.926	2.929	27
$32\bar{1}$	2.882	2.885	19
$20\bar{4}$	2.866	2.862	14
$21\bar{4}$	2.734	2.732	9
131	2.696	2.701	9
$32\bar{3}$	2.669	2.671	6
113	2.632	2.634	8
230	2.602	2.599	10
400	2.454	2.451	6
222	2.424	2.422	2
014	2.396	2.395	7
410	2.364	2.367	28
$42\bar{3}$	2.341	2.340	12
040	2.296	2.297	7
041	2.238	2.237	11
213	2.199	2.200	8
420	2.159	2.160	4
$14\bar{2}$	2.130	2.129	8
$11\bar{5}$	2.106	2.105	3
240	2.078	2.077	19
$13\bar{4}$	2.044	2.044	3
331	2.034	2.033	19
$52\bar{2}$	2.011	2.013	3
142	1.9538	1.9531	8
015	1.9312	1.9347	6
430	1.9099	1.9086	7
204	1.8649	1.8642	2
402	1.8546	1.8544	2
$21\bar{6}$	1.8307	1.8305	7
412	1.8166	1.8169	9
051	1.8003	1.8009	10
242	1.7809	1.7818	11
$44\bar{2}$	1.7751	1.7756	8

TABLE 5

Crystal data for isostructural ammonium lanthanide sulphate monohydrate (Ln = Sm–Yb and Y). Space group $P2_1/c$, $Z = 4$

Metal	a (Å)	b (Å)	c (Å)	β (deg)	V (Å^3)	ρ_{obs} (g cm^{-3})	ρ_{cal} (g cm^{-3})
Eu	10.338(8)	8.455(5)	10.485(9)	119.97(6)	793.9(9)	3.12(4)	3.18
Gd	10.314(4)	8.420(2)	10.432(4)	119.79(2)	786.4(5)	–	3.25
Tb	10.271(4)	8.394(2)	10.396(3)	119.79(2)	779.9(3)	–	3.29
Dy	10.251(4)	8.373(2)	10.374(4)	119.82(3)	772.6(4)	3.31(5)	3.36
Ho	10.221(5)	8.326(2)	10.354(5)	119.79(3)	764.7(5)	–	3.41
Er	10.211(4)	8.306(2)	10.335(4)	119.83(3)	760.5(4)	–	3.45
Tm	10.232(4)	8.295(2)	10.330(4)	119.97(3)	759.6(4)	3.44(4)	3.47
Yb	10.186(8)	8.285(3)	10.292(8)	119.90(6)	752.9(8)	–	3.54
Y	10.237(3)	8.339(2)	10.341(3)	119.77(2)	766.3(3)	2.71(4)	2.75

the structural isomorphism to $RbLn(SO_4)_2 \cdot H_2O$, it can be concluded that the lanthanide ion is eight coordinated in $NH_4Ln(SO_4)_2 \cdot H_2O$ compounds. The ammonium ion behaves as a pseudo alkali metal ion in the salt hydrates and its coordination environment becomes modified by extensive hydrogen bond formation [13]. The observed decrease in the cell volumes of these compounds is in general consistent with the decrease in ionic radius reported for eight coordination: Eu, 1.066 Å; Yb, 1.019 Å [8].

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REFERENCES

1 P.N. Iyer and P.R. Natarajan, J. Less-Common Met., 159 (1990) 1.
2 B. Eriksson, L.O. Larsson, L. Niinisto and U. Skoglund, Inorg. Chem., 13 (1974) 290.
3 N.L. Sarukhanyan, L.D. Iskhakova, I.G. Drobinskaya and V.K. Trunov, Sov. Phys. Crystallogr., 30 (1985) 510.
4 P.N. Iyer and P.R. Natarajan, J. Less-Common Met., 169 (1991) 283.
5 I.M. Kolthoff, P.J. Elving and E.B. Sandell (Eds.), Treatise on Analytical Chemistry, Part II, Vol. 8, Wiley, New York, 1963, p. 51.
6 I. Buzas (Ed.), 4th Int. Conf. on Thermal Analysis, Budapest, July 8–13, 1974, Vol. 3, Heyden, London, 1975, p. 991.
7 H. Tanaka and H. Negita, Thermochim. Acta, 41 (1980) 305.
8 R.D. Shannon, Acta Crystallogr. Sect. A, 32 (1976) 751.
9 M. Falk, Spectrochim. Acta, Part A, 40 (1984) 43.

10 K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 3rd edn., Wiley, New York, 1978, pp. 133, 146, 239.
11 C. Postmus and J.R. Ferrao, J. Chem. Phys., 48 (1968) 3605.
12 N.L. Sarukhanyan, L.D. Iskhakova, V.K. Trunov and V.K. Ilyukhin, Koord. Khim., 10 (1984) 981.
13 A.A. Khan and W.H. Baur, Acta Crystallogr. Sect. B, 28 (1972) 683.