Hydrated Lanthanide Thiocyanates

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INTRODUCTION

The compounds $La(SCN)_3 \cdot 4H_2O$, $La(SCN)_3 \cdot 7H_2O$[1], $Ce(SCN)_3 \cdot 7H_2O$[2], $Sm(SCN)_3 \cdot 6H_2O$[3], $Er(SCN)_3 \cdot 6H_2O$ and $Y(SCN)_3 \cdot 6H_2O$[4] were prepared at the end of nineteenth century. The preparation of $Gd(SCN)_3 \cdot 7H_2O$[5] was also reported, but there is no information concerning the other solid lanthanide thiocyanates.

In the present paper we describe the preparation of the hydrated lanthanide thiocyanates by the reaction of thiocyanic acid and a suspension of the respective rare earth basic carbonates. Compounds with a general formula $Ln(SCN)_3 \cdot 7H_2O$ (Ln = La, Ce, Pr, Nd) and $Ln(SCN)_3 \cdot 6H_2O$ (Ln = Y, Sm to Lu) were prepared. The compounds of praseodymium, neodymium, europium, terbium, dysprosium, holmium, thulium, ytterbium and lutetium are described for the first time. A compound with the composition $Gd(SCN)_3 \cdot 7H_2O$ was not observed. The results of an infra-red spectra study and information about isomorphous relations between the compounds, observed by X-ray powder patterns and properties, are also included.

EXPERIMENTAL

a) LANTHANIDE OXIDES — The 99,9 per cent pure oxides were obtained from *Johnson, Matthey and Co.*, London.

b) THIOCYANIC ACID — Solutions of thyocyanic acid were obtained from solutions of ammonium thiocyanate from a column containing ion exchange resin (Amberlite IR-120 H^+). All the solutions of thiocyanic acid used were freshly prepared.

c) HYDRATED LANTHANIDE THIOCYANATES — The lanthanide oxide (ca. 0,01 mol) in each case was dissolved in hydrochloric acid, and the solution diluted. Lanthanide basic carbonate was precipitated from a homogeneous solution by the addition of urea and boiling the resulting solution. The product was filtered and washed with hot water until chloride-free. A water suspension of the basic carbonate was treated with dilute thiocyanic acid (a little excess of the basic carbonate in relation to the acid necessary was used). The solution was filtered, evaporated in a water bath until about 30 ml was left and the remaining solution evaporated in a vacuum desiccator, until dry. The crystals obtained were ground, maintained in the desiccator over calcium chloride and then analysed.

d) ANALYTICAL DATA — The lanthanides were determined by the usual oxalate method, and water by the Karl-Fischer procedure. For the determination of thiocyanate ions an aqueous solution of the compound was passed through a cathionic resin (Amberlite

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IR–120H$^+$) and the thiocyanic acid titrated with standard sodium hydroxyde solution, using methylred as an indicator. The analytical results are summarized in TABLE 1.

TABLE 1

SUMMARY OF ANALYTICAL RESULTS

COMPOUND	Formula Weight	ANALYSIS					
		Metal		Thiocyanate		Water	
		Theor. (%)	Exp. (%)	Theor. (%)	Exp. (%)	Theor. (%)	Exp. (%)
Pr $(SCN)_3 . 7H_2O$......	441.3	31.93	32.09	39.48	39.61	28.58	28.48
Nd $(SCN)_3 . 7H_2O$......	444.6	32.44	32.97	39.18	39.22	28.36	28.55
Eu $(SCN)_3 . 6H_2O$......	434.3	34.98	34.63	40.11	40.05	24.88	24.98
Gd $(SCN)_3 . 6H_2O$......	439.6	35.77	35.70	39.63	39.15	24.58	24.38
Tb $(SCN)_3 . 6H_2O$......	441.3	36.01	36.16	39.48	39.21	24.49	24.09
Dy $(SCN)_3 . 6H_2O$......	444.8	36.53	36.35	39.17	39.02	24.30	24.74
Ho $(SCN)_3 . 6H_2O$......	447.3	36.87	37.15	38.95	38.57	24.16	23.72
Tm$(SCN)_3 . 6H_2O$......	451.3	37.43	37.12	38.60	38.20	23.95	23.97
Yb $(SCN)_3 . 6H_2O$......	455.4	37.99	38.15	38.25	37.91	23.73	23.85
Lu $(SCN)_3 . 6H_2O$......	457.3	38.26	38.35	38.10	37.77	23.63	23.20

e) INFRA–RED SPECTRA — The infra-red spetra were determined with a Perkin-Elmer Model 137 Double Beam Recording Spectrophotometer, using Nujol suspensions between rock salt plates.

f) X–RAY DIFFRACTION PATTERNS — The patterns were obtained with a Norelco unit, with Buerger powder camera (114,6 mm). The hygroscopic substances were enclosed, after grinding, in Lindemann glass capillary tubes (0,5 mm diameter). The samples were exposed to Cu–Kα radiation (λ = 1.5148 Å) at room temperature, for about 20 hours.

g) MORPHOLOGICAL AND OPTICAL MEASUREMENTS — Morphological measurements were made (only in the Yb$(SCN)_3 \cdot 6H_2O$ crystals) in the one-circle optical goniometer. The refractive indexes were determined by the immersion method using a Cargille set of liquids. The axial angle 2V was measured either directly in the U-stage or obtained from optical data plotted in stereographic net.

RESULTS AND DISCUSSION

a) INFRA–RED SPECTRA — It has been suggested that the position of the band assigned to the C—N stretching frequency (ν_1) depends upon the nature of the bonding of the ligand to the central atom, and that the ionic or covalent character of the metal-thiocyanate bond may affect the frequency of this group [6]. For extreme ionic salts this band is found near 2000 cm^{-1}, for example KSCN — 2066 cm^{-1}[7], NaSCN — 2020 cm^{-1} and Ba$(SCN)_2 \cdot 2H_2O$ — 2060 cm^{-1}[8]. On the other hand, thiocyanate co-ordinates to metal-ions with the formation of M–NCS or M–SCN bonds or even as a difunctional ligand, where the SCN group is a bridge between two metal-ions [6, 9]. In these latter cases the frequencies are generally at higher wave numbers [10]. (See also references 6 and 9 where many examples are given).

The espectra of the lanthanide thiocyanates were determined in the infra-red region. The peak assigned to C—N stretching was observed at 2020 cm^{-1} for the compounds of neodymium, erbium and ytterbium; at 2040 cm^{-1} for yttrium and thullium, and 2030cm^{-1}

for the other compounds; giving us the idea that the bond of the SCN group is essentially ionic in character and that the metal-ion is co-ordinated to water molecules.

b) X-RAY POWDER PATTERNS. — The X-ray powder diffraction patterns showed that the compounds of the general formula $Ln(SCN)_3 \cdot 7H_2O$ are isomorphous (See TABLE 2), and that the compounds of formula $Ln(SCN)_3 . 6H_2O$ also form another series of isomorphous substances (see TABLES 3 and 4).

TABLE 2

X-RAY POWDER DIFFRACTION PATTERNS OF THE COMPOUNDS OF GENERAL FORMULA $Ln(SCN)_3 \cdot 7H_2O$

Visual average intensities I	La d(Å)	Ce d(Å)	Pr d(Å)	Nd d(Å)
1	13.2	13.2	—	13.2
1	—	—	—	11.5
1	—	—	—	8.7
2	—	7.7	7.9	7.8
3	7.4	7.4	7.4	7.4
4	—	6.58	6.53	6.61
8	6.32	6.39	6.36	6.30
4	6.09	6.18	6.19	—
2	—	5.03	5.05	4.99
3	4.81	4.80	4.78	4.78
6	4.18	4.18	4.17	4.16
10	4.03	4.07	4.04	4.03
3	3.53	3.55	3.54	3.51
2	3.43	3.45	3.44	3.43
1	—	3.37	3.30	3.28
1	3.20	3.24	3.22	3.22
1	—	3.13	3.13	3.13
1	3.03	3.03	3.09	3.02
2	2.98	2.98	2.98	—
1	—	2.90	2.89	2.87
1	—	2.81	2.81	2.80
5	2.76	2.77	2.76	2.75
2	2.70	2.71	2.71	—
3	—	2.67	2.67	2.65
3	2.59	2.59	2.59	2.57
4	2.54	2.54	2.53	2.53
1	2.40	2.42	2.40	2.41
2	2.37	2.36	2.36	2.38
1	—	2.34	2.34	2.33
2	2.25	2.25	2.25	2.24
2	2.20	2.20	2.20	2.19
1	2.14	2.14	2.14	2.13
2	2.07	2.06	2.06	2.05
1	2.03	2.04	2.04	2.02
2	1.96	1.96	1.95	1.95
1	1.903	1.913	1.910	—
1	1.869	1.871	1.864	—
4	1.828	1.836	1.833	1.824
3	—	1.795	1.791	1.783
2	1.780	1.777	1.775	1.768
1	1.735	1.734	1.726	1.722
2	—	1.697	1.688	1.681
3	1.673	1.668	1.664	1.658
1	1.636	1.652	1.643	—
3	1.612	1.612	1.608	1.601
2	1.577	1.783	1.579	1.571
2	1.554	1.552	1.551	1.546
2	1.512	1.520	1.517	1.518
2	—	1.296	1.288	1.285
2	1.192	1.190	1.189	1.181

Table 3

X--Ray Powder' Diffraction Patterns of Compounds of General Formula $Ln(SCN)_3 \cdot 6H_2O$

Visual average intensities I	Sm d(Å)	Eu d(Å)	Gd d(Å)	Tb d(Å)	Dy d(Å)
2	—	—	—	14.8	—
2	—	—	—	11.8	—
2	—	—	—	8.3	—
8	7.7	7.6	7.5	7.7	7.6
10	6.22	6.13	6.12	6.18	6.12
1	6.00	5.93	5.92	5.95	5.86
5	5.43	5.41	5.39	—	5.40
8	4.38	4.36	4.37	4.38	4.34
4	4.14	4.14	4.13	4.14	4.10
4	3.98	3.97	3.96	3.99	3.95
8	3.77	3.74	3.74	3.75	3.73
8	3.64	3.63	3.64	3.65	3.61
2	3.49	3.48	3.46	3.51	3.46
2	3.29	3.28		3.28	3.25
2	3.10	3.07	—	3.09	3.08
3	3.00	2.99	2.98	2.99	2.96
2	2.73	2.72	—	2.73	—
4	2.68	2.67	2.65	2.68	2.66
5	2.57	2.57	2.55	2.57	2.55
4	2.44	2.44	2.42	2.43	2.42
1	2.35	2.35	2.34	2.35	2.34
2	2.31	2.31	2.29	2.31	2.30
2	2.28	2.28	2.25	2.28	2.28
6	2.21	2.21	2.19	2.21	2.21
5	2.09	2.09	2.10	2.10	2.08
2	2.04	2.04	2.02	2.04	2.02
2	—	1.866	1.858	1.863	1.856
3	1.834	1.829	1.818	1.828	1.812
2	1.762	1.761	1.754	1.762	1.754
2	1.736	1.737	1.728	1.737	1.728
1	1.705	1.701	1.692	1.698	1.691
2	1.673	1.672	1.667	1.673	1.665
2	1.591	1.591	—	1.587	—
3	1.459	1.456	—	1.461	1.452
3	1.441	1.438	1.432	1.438	1.432

TABLE 4

X-RAY POWDER DIFFRACTION PATTERNS OF THE COMPOUNDS OF GENERAL FORMULA $Ln(SCN)_3 \cdot 6H_2O$

Visual average intensities I	Y d(Å)	Ho d(Å)	Er d(Å)	Tm d(Å)	Yb d(Å)	Lu d(Å)
2	8.5	—	—	—	—	8.3
8	7.7	7.7	7.7	7.6	7.6	7.6
10	6.12	6.09	6.17	6.11	6.15	6.11
1	5.96	5.91	5.89	5.82	5.85	5.85
5	5.41	—	5.41	5.40	5.39	5.41
1	4.57	4.59	4.59	4.54	4.56	4.56
8	4.35	4.35	4.36	4.35	4.36	4.34
4	4.13	4.13	4.12	4.12	4.09	4.10
4	3.95	3.95	3.94	3.93	3.92	3.92
8	3.74	3.71	3.74	3.71	3.72	3.70
8	3.61	3.61	3.60	3.60	3.60	3.60
2	3.46	3.45	3.46	3.45	3.44	3.45
2	3.26	3.26	3.25	3.25	3.25	3.25
2	3.04	3.06	3.06	3.06	3.04	3.03
3	2.97	2.96	2.97	2.97	2.96	2.95
1	2.79	—	2.79	2.80	2.79	2.78
2	2.72	—	2.72	2.72	—	2.70
4	2.66	—	2.66	2.65	2.64	2.65
5	2.56	2.55	2.56	2.55	2.55	2.54
4	2.42	2.41	—	2.42	2.42	2.41
1	2.35	2.36	2.36	2.34	2.35	2.34
2	2.30	2.30	2.30	2.30	2.29	2.28
2	2.25	2.26	—	2.25	2.24	2.24
6	2.20	2.19	2.19	2.18	2.19	2.18
1	2.15	2.14	2.15	2.14	2.14	2.13
5	2.09	2.11	2.11	2.09	2.08	2.08
2	2.03	2.03	2.03	2.02	2.02	2.02
2	1.862	1.854	1.855	1.860	1.857	1.853
3	1.811	1.812	1.807	1.805	1.805	1.801
2	1.768	1.758	1.752	—	1.748	1.748
2	1.727	1.729	1.730	1.721	1.721	1.719
1	1.693	1.689	1.690	1.686	1.686	1.684
2	1.663	1.665	1.666	1.659	1.658	1.659
2	1.590	1.586	—	1.579	1.583	1.576
2	1.573	1.570	1.573	1.573	1.569	1.566
2	1.554	1.555	—	1.548	1.551	1.546
2	1.484	1.487	1.491	1.487	1.486	1.482
3	1.486	1.474	1.472	1.472	1.467	1.466
3	1.453	1.454	1.452	1.449	1.446	1.444
3	1.431	1.429	1.429	1.430	1.428	1.424
3	1.373	1.373	1.373	1.370	1.367	1.367
2	1.278	1.280	1.276	1.274	1.276	1.273
2	1.223	1.224	1.222	1.220	1.220	1.217
2	1.178	1.178	—	1.175	1.175	1.175
3	1.013	—	1.004	1.002	1.000	0.999
2	—	—	—	0.966	0.968	0.962
2	—	—	—	0.932	0.931	0.928
2	—	—	—	0.912	0.911	0.909

c) MORPHOLOGY AND OPTICAL PROPERTIES — The substances can be separated into two distinctive groups of crystals: the first group includes the compounds of general formula $Ln(SCN)_3 \cdot 7H_2O$. Although morphological measurements were relatively inaccurate, the optical orientation in this group is entirely different from the second one, but the symmetry seems to be similar (see below). Two pairs of faces are well developed in a zone [001] intercepting in an angle of about 65°.

$X \wedge C$ (elongation) = small.

Pl. O. A. // c cut the obtuse $(hko) \cdot (h\bar{k}o)$ angle. (See Fig. 1).

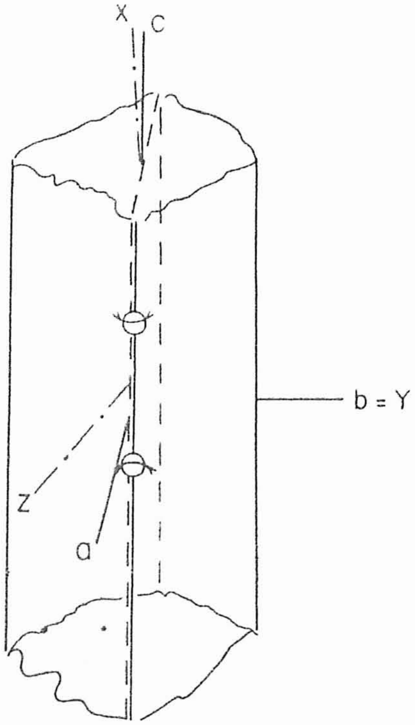

Fig. 1

The monoclinic symmetry is enhanced by a week but still detectable inclined dispersion of the optical axis. A summary of the optical constants for the compounds of general formula $Ln(SCN)_3 \cdot 7H_2O$ is found in the TABLE 5.

TABLE 5

OPTICAL CONSTANTS OF THE COMPOUNDS OF GENERAL FORMULA $Ln(SCN)_3 \cdot 7H_2O$

Ln	N_X	N_Y	N_Z	N_Z-N_X	$2V_Z$	Disp.
La	1.606	1.615	1.675	0.069	45°	inclined
Ce	1.608	1.617	1.676	0.069	44°	inclined
Pr	1.608	1.618	1.676	0.068	44°	inclined
Nd	1.609	1.618	1.677	0.068	45°	inclined

The second group includes the compounds of general formula $Ln(SCN)_3 \cdot 6H_2O$. Only the $Yb(SCN)_3 \cdot 6H_2O$ crystals were bounded by faces suitable for universal-stage angular measurements and determination of the optical indicatrix.

The ytterbium thiocyanate crystals are elongated parallel to b. In the zone [010] two pairs of faces are best developed intercepting in angle of about 114° (66°). Two vertical prisms (110) and (120) and the angles $(100) \cdot (110) = 40^\circ$ and $(100) \cdot (120) = 58^\circ$ were also observed. The optical plane containing Z and X is normal to the elongation and the two velocities are inclined to the face normals:

$$X \wedge (100) = 35^\circ$$

$$X \wedge (001) = 21^\circ$$

$$Z \wedge (001) = 59^\circ$$

$$Z \wedge (\bar{1}00) = 55^\circ$$

In this way the complete orientation data becomes:

$$Y = b \text{ (elongation)}$$

$$X \wedge a = 59^\circ$$

$$Z \wedge c = 35^\circ$$

So, the monoclinic optical symmetry is proved. (See Figures 2 and 3).

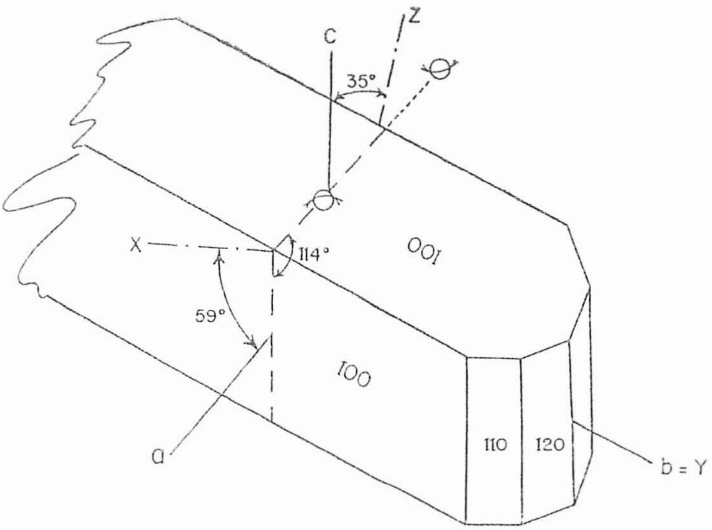

Fig. 2

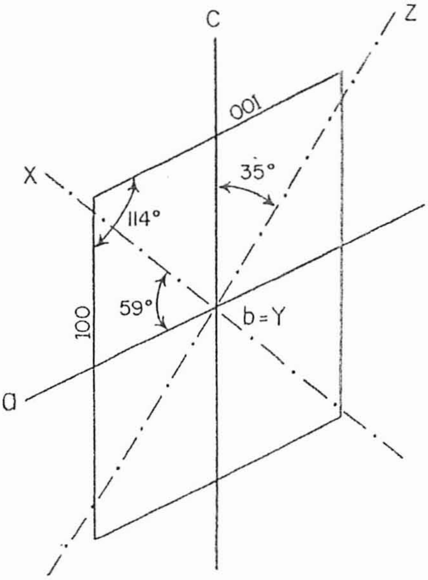

Fig. 3

Since the crystals were generally somewhat dissolved and rounded, the conditions of observation for the remaining substances were precarious. Nevertheless it would be safer to state that the orientation is the same for the whole series in this second group, with a variation in angular measurements of not more than 5°. TABLE 6 contains a summary of the optical constants of this group.

Table 6

Optical Constants of the Compounds of General Formula $Ln(SCN)_3 \cdot 6H_2O$

Ln	N_X	N_Y	N_Z	N_Z-N_X	$2V_Z$	Disp.
Y	1.562	1.594	1.656	0.096	75°	V > r
Sm	1.567	1.598	1.660	0.093	73°	V > r
Eu	1.564	1.598	1.660	0.096	75°	V > r
Gd	1.564	1.597	1.660	0.096	74°	V > r
Tb	1.568	1.599	1.660	0.092	73°	V > r
Dy	1.569	1.601	1.662	0.093	74°	V > r
Ho	1.568	1.602	1.662	0.094	76°	V > r
Er	1.570	1.604	1.666	0.096	75°	V > r
Tm	1.572	1.605	1.663	0.091	76°	V > r
Yb	1.572	1.605	1.664	0.092	75°	V > r
Lu	1.572	1.604	1.664	0.092	74°	V > r

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