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Synthesis, characterization, properties and thermal study of lanthanoid isothiocyanate complexes with 2,6-lutidine-*N*-oxide (2,6-LNO)

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Abstract

Lanthanoid isothiocyanate complexes of general formula $Ln(NCS)_3(2,6\text{-}LNO)_3(H_2O)_n$, where n is 3, for Ln is La, n is 1, for Ln is Ce–Nd and Eu–Tb, and n is 0 for Ln is Tm, Lu, Y, were synthesized and characterized. They behave as non-electrolytes in acetonitrile. The anion is bonded through the nitrogen and 2,6-LNO through the oxygen. The nephelauxetic parameter, covalent factor and Sinha's parameter and also the oscillator strength in acetonitrile solution were calculated from the neodymium absorption spectra. A C_{3v} symmetry and a monocaped trigonal prismatic geometry, with the water molecule located on the rotation axis, was deduced from the emission spectrum of the europium compound. The similarities between the emission spectra of the europium complex and the europium-doped lanthanum and lutetium adducts suggests that the central ions are also involved in a C_{3v} symmetry. The TG, DTG and DSC measurement were recorded in dynamic air and nitrogen atmospheres and interpreted.

INTRODUCTION

Only a few papers dedicated to lanthanoid complexes containing 2,6-LNO can be found in the literature. The first, from our laboratory [1], describes some nitrate, perchlorate and chloride compounds: $Ln(NO_3)_3 \cdot 4(2,6\text{-}LNO)$, $Ln(ClO_4)_3 \cdot 8(2,6\text{-}LNO)$ and $LnCl_3 \cdot 3(2,6\text{-}LNO)$ (Ln is Y, La, Nd, Gd, Er). Another publication [2] describes complexes with compositions $Ln[(2,6\text{-}LNO)_4(ClO_4)_3] \cdot 2H_2O$ (Ln is La, Pr, Nd) and $Ln(2,6\text{-}LNO)_2(ClO_4)_3$ (Ln is Sm, Ho, Er, Yb, Y). The third [3] considers the iodides of formulae $Ln(2,6\text{-}LNO)_5I_3$ (Ln is La, Tb, Yb), $Ln(2,6\text{-}LNO)_4I_3$ (Ln is Pr, Nd) and $Ln(2,6\text{-}LNO)_{4.5}I_3$ (Ln is Er). The most recent deals with the species $[La(2,6\text{-}LNO)_8]^{3+}$ [4].

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In this article, the 2,6-LNO isothiocyanate complexes are described and characterized by microanalytical procedures, conductance measurements in acetonitrile, IR spectra, absorption spectra of the neodymium compound, the emission spectrum of the europium complex and emission spectra of the europium-doped lanthanum and lutetium complexes, and by a thermoanalytical study.

EXPERIMENTAL

The ligand was prepared from 2,6-lutidine (Aldrich) by reaction with hydrogen peroxide in glacial acetic acid, according to a procedure adapted from Ochiai's synthesis of pyridine-*N*-oxide [5]. The compound was purified by distillation at 115–118°C under 2 mm Hg pressure.

For the preparation of the complexes, ethanolic solutions of the hydrated thiocyanates and of the ligand (molar ratio 1:3) were mixed and treated with anhydrous ethyl ether in order to precipitate the compounds.

Crystals were collected and dried in vacuo over anhydrous calcium chloride. For the preparation of the doped lanthanum and lutetium complexes, 2% of the europium thiocyanate was added to the respective salts before addition of the ligand.

Analysis and measurements

The lanthanoid was determined by EDTA titration [6]. Carbon, hydrogen and nitrogen were determined by standard microanalytical procedures. Conductance measurements were performed with a Leeds and Northrup resistance box, using a pointer galvanometer and conductivity cell with $K_c = 0.10708\ \text{cm}^{-1}$, at 25.00 ± 0.02°C. IR spectra were recorded on a Perkin–Elmer 1750 spectrophotometer using KBr pellets and Nujol mulls between KBr plates. Electronic absorption spectra of the neodymium compound were registered in a Cary 2300 apparatus at room temperature and at 77 K in silicone mulls and acetonitrile solution. The emission spectra of the europium compound, and of the lanthanum and lutetium Eu^{3+}-doped compounds were recorded in a Zeiss ZFM-4 spectrofluorimeter at 77 K. The refractive index of the neodymium solution was determined in an Abbé-type, Bausch and Lomb refractometer. TG and DTG analyses were performed using a Perkin-Elmer TGA system, with a scanning rate of $10.0\ \text{K min}^{-1}$ in dynamic air or nitrogen atmospheres. DSC analyses were determined in a Mettler System TA 4000 in dynamic nitrogen atmosphere (gas flow $60\ \text{ml min}^{-1}$).

RESULTS AND DISCUSSION

Table 1 contains a summary of the analytical results and conductance data, which indicates a non-electrolyte behaviour in acetonitrile [7].

TABLE 1

Summary of analytical data and conductance measurements in acetonitrile

Compound	Analysis/%									
	Lanthanide		Carbon		Hydrogen		Nitrogen		Conductance	
	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	Conc/mM	Λm[a]
$La(NCS)_3(2,6\text{-}LNO)_3(H_2O)_3$	19.17	19.32	39.78	39.94	4.59	4.41	11.60	11.64	0.98	31
$Ce(NCS)_3(2,6\text{-}LNO)_3(H_2O)$	19.96	19.87	41.07	40.97	4.16	4.18	11.97	11.70	1.04	34
$Pr(NCS)_3(2,6\text{-}LNO)_3(H_2O)$	20.05	20.02	41.03	40.59	4.16	4.17	11.96	11.62	1.04	33
$Nd(NCS)_3(2,6\text{-}LNO)_3(H_2O)$	20.43	20.47	40.83	40.36	4.14	4.10	11.90	11.83	0.98	26
$Eu(NCS)_3(2,6\text{-}LNO)_3(H_2O)$	21.29	21.19	40.39	39.95	4.09	4.07	11.78	11.72	0.99	28
$Gd(NCS)_3(2,6\text{-}LNO)_3(H_2O)$	21.87	21.55	40.09	39.54	4.06	4.04	11.69	11.49	0.98	29
$Tb(NCS)_3(2,6\text{-}LNO)_3(H_2O)$	22.44	22.51	40.00	39.46	4.06	4.05	11.66	11.22	0.95	25
$Tm(NCS)_3(2,6\text{-}LNO)_3$	23.70	23.84	40.45	40.24	3.81	3.76	11.79	11.64	0.96	25
$Lu(NCS)_3(2,6\text{-}LNO)_3$	24.35	24.23	40.11	39.62	3.79	3.80	11.69	11.64	1.06	26
$Y(NCS)_3(2,6\text{-}LNO)_3$	14.05	13.56	45.56	44.39	4.30	4.62	13.28	13.66	1.05	46

[a] $\Lambda m = \Omega^{-1}\ cm^2\ mol^{-1}$.

IR spectra show that in the region corresponding to ν(NO) (1244 cm^{-1} for the free ligand), splittings and shifts to lower frequencies are observed for the cerium–neodymium and europium–terbium compounds (1244$_s$ (strong) and 1222$_{vs}$ (very strong) cm^{-1}); for the lanthanum, thulium and lutetium compounds only a single shift was observed (1222–1226$_{vs}$ cm^{-1}), δ(NO) being practically unchanged (841$_s$ cm^{-1}), except for the complexes of europium, gadolinium and terbium where a splitting (853$_{sh}$ and 840$_s$ cm^{-1}) was observed; γ(CH) is slightly shifted towards higher frequencies (778$_s$ cm^{-1} for the free ligand as compared to 787 cm^{-1} for the complexes. For the anions, the vibration modes ν(CN) and δ(NCS) were observed at 2075–2050$_s$ and 490–476$_m$ cm^{-1}. The observed frequencies are indicative of coordination of NCS$^-$ through the nitrogen and of 2,6-LNO through the oxygen. Intense and less intense water bands were observed in the lanthanum complex and in the complexes containing the water molecule, respectively.

Figure 1 shows the absorption spectra of the neodymium compound in the $^2G_{7/2}$, $^4G_{5/2} \leftarrow {}^4I_{9/2}$ and $^2P_{1/2} \leftarrow {}^4I_{9/2}$ transition regions. The number of bands (11) is the 77 K spectrum indicates that Nd^{3+} ions are not involved in a cubic site. The nephelauxetic parameter $\beta_1 = 23137/23468 = 0.986$, $\beta_2 = 17053/17329 = 0.984$, $\bar{\beta} = 0.985$ was calculated from the solid state spectrum at room temperature. The covalent factor [8], $b^{1/2} = 0.087$ and Sinha's parameter [9] $\delta(\%) = 1.52$, calculated from $\bar{\beta}$, are indicative of essentially electrostatic bonds between Nd^{3+}, and the ligands. The spectrum is slightly different from that in acetonitrile solution. The oscillator strength [10] was calculated as $P = 29.8 \times 10^6$.

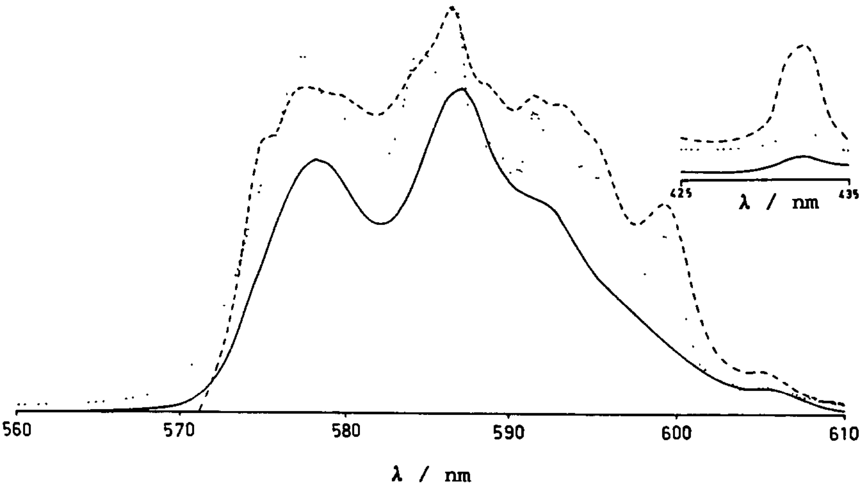

Fig. 1. Absorption spectra of the neodymium complex: – – –, at room temperature; · · ·, at 77 K; and ——, in acetonitrile solution.

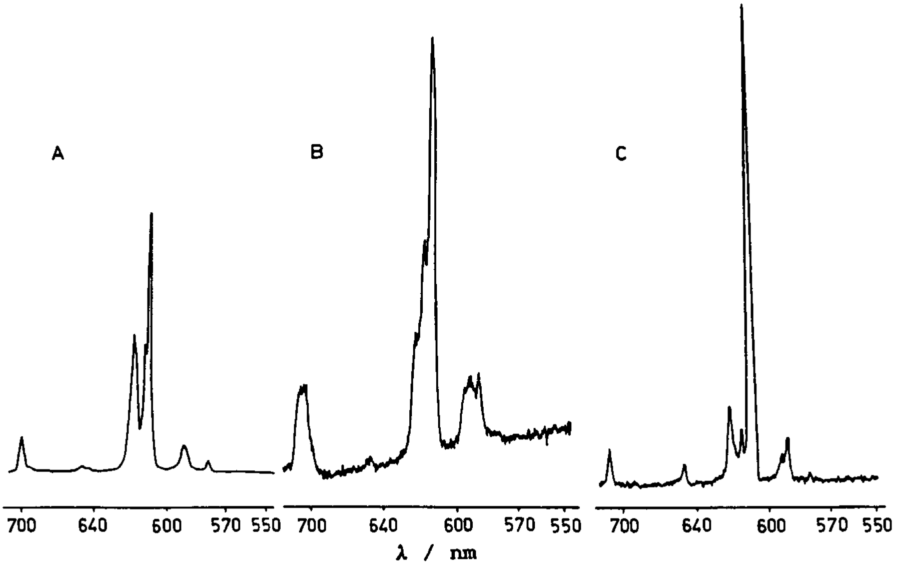

Fig. 2. Emission spectra at 77 K. A, europium complex; B, lanthanum complex doped with europium; C, lutetium complex doped with europium.

The fluorescence spectra of the europium compound and of the europium-doped lanthanum and lutetium compounds are presented in Fig. 2. The spectra of A and C were interpreted in terms of a C_{3v} symmetry, because they present a $^5D_0 \rightarrow {}^7F_0$ transition, three peaks due to $^5D_0 \rightarrow {}^7F_1$ (species A_1 and E) and three peaks due to $^5D_0 \rightarrow {}^7F_2$ (one A_1 and two E species) [11]. The lanthanum spectrum presents the same peaks, but that due to a $^5D_0 \rightarrow {}^7F_0$ transition is not clear.

Figures 3–6 contain some representative TG and DTG curves in dynamic air and nitrogen atmospheres. Tables 2 and 3 show TG and DSC data for the complexes in dynamic nitrogen atmosphere and Table 4 gives the TG

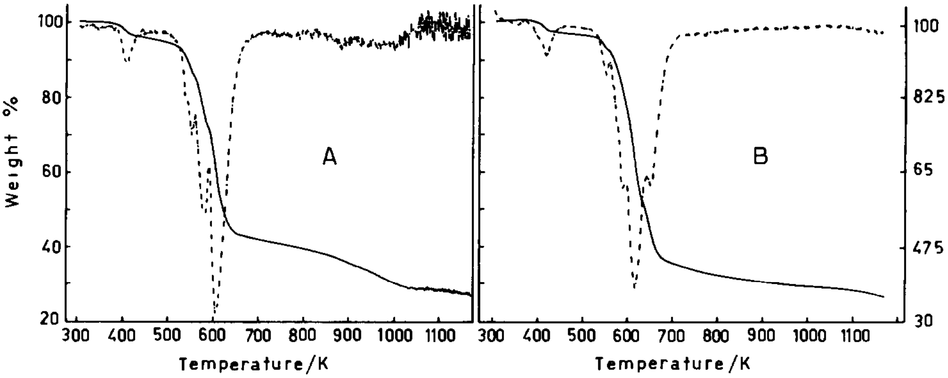

Fig. 3. TG and DTG analyses of the lanthanum compound: A, air atmosphere; B, nitrogen atmosphere.

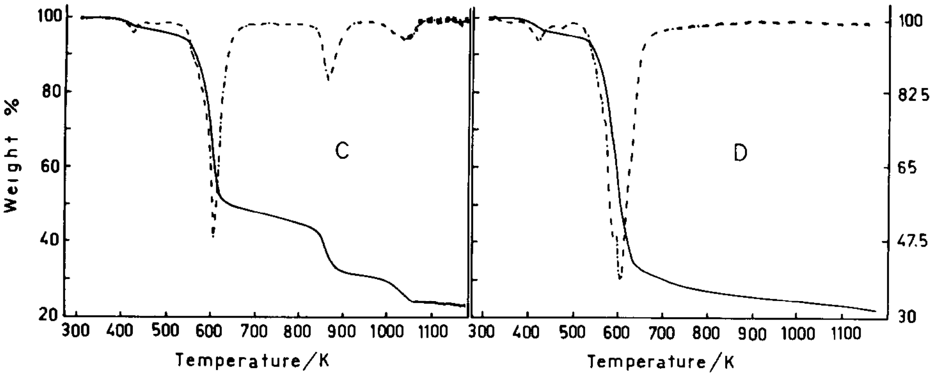

Fig. 4. TG and DTG analysis of the cerium compounds: C, air atmosphere; D, nitrogen atmosphere.

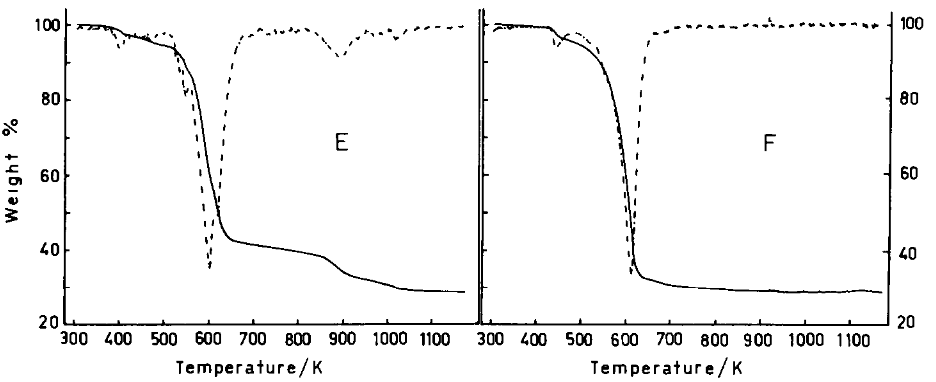

Fig. 5. TG and DTG analysis of the neodymium compound: E, air atmosphere; F, nitrogen atmosphere.

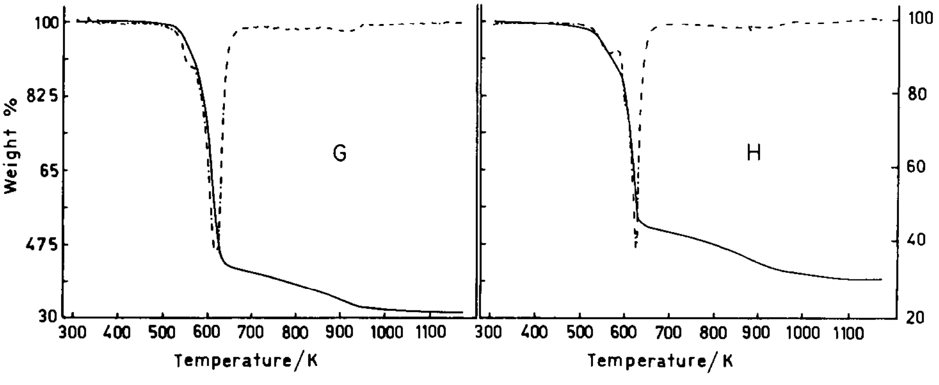

Fig. 6. TG and DTG analysis of the thulium compound: G, air atmosphere; H, nitrogen atmosphere.

TABLE 2

TG data (dynamic nitrogen atmosphere)

Ln	Weight loss of residue/%		Temperature/K	Attribution
	Theor.	Exp.		
La	7.34	6.3	373–550	$-3H_2O$ (two steps)
	50.15	49.6	550–683	−3LNO
	25.40	36.0	-1183	(La_2S_3 + Carbon)
Ce	2.57	3.6	373–493	$-H_2O$
	52.64	54.7	493–648	−3LNO
	26.81	31.6	-1183	(Ce_2S_3 + Carbon)
Pr	2.56	3.2	373–416	$-H_2O$
	52.58	56.7	416–600	−3LNO
	26.91	31.6	-1183	(Pr_2S_3 + Carbon)
Nd	2.55	2.7	377–428	$-H_2O$
	52.32	65.0	460–639	−3LNO
	27.24	28.7	-1183	(Nd_2S_3)
Eu	2.52	2.7	383–423	$-H_2O$
	51.76	48.6	423–627	−3LNO
	28.05	28.4	-1183	Eu_2S_3
Gd	2.50	2.4	350–385	$-H_2O$
	51.38	58.6	440–639	−3LNO
	28.56	27.6	-1183	Gd_2S_3
Tb	2.50	3.0	352–393	$-H_2O$
	51.26	63.1	467–604	−3LNO
	28.72	29.1	-1183	Tb_2S_3
Y	56.78	56.0	520–669	−3LNO
	21.06	23.2	-1183	Y_2S_3
Tm	51.84	53.5	506–667	−3LNO
	30.46	30.4	-1183	Tm_2S_3
Lu	51.40	53.5	534–641	−3LNO
	31.03	29.9	-1183	Lu_2S_3

data for the compounds in dynamic air atmosphere. In nitrogen, the complexes initially lose water (except for Tm, Lu and Y), then melt, lose the ligands with carbonization in exothermic reactions and finally give lanthanide sulphides as residues. In some cases carbon is also observed in the residues. The existence of sulphide was confirmed by the characteristic odour of hydrogen sulphide when heated with dilute hydrochloric acid. In air, the evolution of water and decomposition of LNO occurs. The final residues are oxo-sulphates as indicated (Table 4). The existence of sulphates was confirmed by IR spectra, showing a strong band at 1112 cm^{-1}

TABLE 3

DSC data (dynamic nitrogen atmosphere)

Ln	Temperature/ K	Attribution	Peak temp./K	ΔH/kJ mol^{-1}
La	353–412	$-3H_2O$ (two peaks)	380	88.4
			402	11.2
	453–466	Melting	465	22.1
	573–693	−3LNO (two peaks)	588	−163.2
			626	−274.8
Ce	373–448	$-H_2O$	416	71.6
	456–466	Melting	461	3.9
	528–613	−3LNO	585	−243.5
Pr	373–420	$-H_2O$	411	105.4
	433–463	Melting + dec.	457	65.3
	573–643	−3LNO (three peaks)	591	−71.7
			603	−17.6
			631	−16.0
Nd	373–418	$-H_2O$	409	87.5
	423–463	Melting (two peaks)	450	
			457	84.0
	543–623	−3LNO	597	
			605	−187.1
Eu	373–400	$-H_2O$	392	83.5
	413–468	Melting	461	77.1
	526–598	−3LNO (two peaks)	558	
			581	−175.6
Gd	373–398	$-H_2O$	391	90.6
	443–483	Melting	473	43.1
	572–618	−3LNO (two peaks)	585	
			604	−105.0
Tb	353–385	$-H_2O$	379	93.7
	463–503	Melting	491	41.8
	568–623	−3LNO (two peaks)	586	
			608	−170.0
Y	513–533	Melting	528	42.6
	533–618	−3LNO (two peaks)	572	
			598	−105.4
Tm	503–543	Melting	525	61.3
	543–621	−3LNO (two peaks)	577	−116.9
			605	−18.1
Lu	513–553	Melting	637	46.7
	553–598	−3LNO (two peaks)	571	
			591	−153.1

TABLE 4

TG data (dynamic air atmosphere)

Ln	Weight loss of residue/%		Temperature/K	Attribution
	Theor.	Exp.		
La	7.34	6.4	373–527	$-3H_2O$
	50.15	50.0	527–660	$-3LNO$
	27.58	27.1	–1183	$0.5La_2O_2SO_4$
Ce	2.57	2.8	353–527	$-H_2O$
	52.64	53.9	540–843	$-3LNO$
	29.10	31.6	843–907	$0.5Ce_2O_2(SO_4)$
	24.53	23.0	–1183	CeO_2
Pr	2.56	2.5	397–427	$-1H_2O$
	52.58	56.8	427–653	$-3LNO$
	34.90	32.7	653–820	$0.5Pr_2O(SO_4)_2$
	29.20	31.3	–1183	$0.57Pr_2O_2(SO_4)$
Nd	2.55	2.7	378–402	$-H_2O$
	52.32	55.0	402–659	$-3LNO$
	35.17	38.4	659–840	$0.5Nd_2O(SO_4)_2$
	29.50	29.2	–1183	$0.5Nd_2O_2(SO_4)$
Eu	2.52	2.5	369–411	$-H_2O$
	51.76	48.3	411–626	$-3LNO$
	35.90	35.4	626–914	$0.5Eu_2O(SO_4)_2$
	30.29	30.0	–1183	$0.5Eu_2O_2(SO_4)$
Gd	2.50	26.2	350–386	$-1H_2O$
	51.38	52.2	386–614	$-3LNO$
	36.30	36.7	614–862	$0.5Gd_2O(SO_4)_2$
	30.78	28.0	–1183	$0.5Gd_2O_2(SO_4)$
Tb	2.50	2.6	358–389	$-1H_2O$
	51.26	52.2	484–651	$-3LNO$
	36.58	37.0	651–871	$0.5Tb_2O(SO_4)_2$
	30.95	30.3	–1183	$0.5Tb_2O_2(SO_4)$
Y	56.78	54.0	420–631	$-3LNO$
	33.35	34.0	631–857	$0.5Y_2O(SO_4)_2$
	23.52	22.5	–1183	$0.5Y_2O_2SO_4)$
Tm	51.84	53.5	506–667	$-3LNO$
	32.72	31.7	–1183	$0.5Tm_2O_2(SO_4)$
Lu	51.40	52.5	498–636	$-3LNO$
	33.08	32.0	–1183	$0.5Lu_2O_2(SO_4)$

(ν_3) [12] and also by reaction of the residues with hydrochloric acid followed by addition of barium nitrate. In all cases, white precipitates were observed. The existence of thiocyanate ions in the residue obtained at about 620 K was confirmed by the strong band (ν(CN)) at 2067 cm^{-1} [12].

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