

# Synthesis and Spectroscopic, Diffractometric, and Magnetic Analysis of Lanthanide Compounds with Thiocyanate and Hexamethylenetetramine

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**Summary.** New complex salts of lanthanide thiocyanates with hexamethylenetetramine of the general formula  $Ln(NCS)_3 \cdot 2[N_4(CH_2)_6 \cdot nH_2O]$ , where  $Ln = La, Pr, Nd, Sm, Gd, Dy, Er$  and  $n = 0-10$ , have been analyzed. IR spectra have been obtained in the range of  $200-4000\text{ cm}^{-1}$ , frequencies of vibrations of low and high hydration state compounds have been analyzed, and differences between the structures of the coordination spheres of these salts are demonstrated. Diffractometric examinations and measurements of the magnetic susceptibility of several salts have been performed.

**Keywords.** Lanthanides; Complexes; Hexamethylenetetramine; IR spectra; Thiocyanates.

## Synthese und spektroskopische, diffraktometrische und magnetische Untersuchungen von Verbindungen der Lanthaniden mit Rhodanid und Hexamethylenetetramin

**Zusammenfassung.** Neue Komplexsalze der Lanthaniden mit Rhodanid und Hexamethylenetetramin mit der allgemeinen Formel  $Ln(NCS)_3 \cdot 2[N_4(CH_2)_6] \cdot nH_2O$  ( $Ln = La, Pr, Nd, Sm, Gd, Dy, Er$ ;  $n = 0-10$ ) wurden untersucht. Die IR-Spektren der Verbindungen im Bereich von  $200-4000\text{ cm}^{-1}$  wurden aufgenommen. Die Schwingungsfrequenzen hoch- und niederhydrierter Verbindungen wurden analysiert und die Unterschiede in der Struktur der Koordinationssphäre bestimmt. An einigen Komplexen wurden diffraktometrische Untersuchungen und Messungen der magnetischen Suszeptibilität durchgeführt.

## Introduction

The present work demonstrates the results of IR spectroscopic, diffractometric and magnetic analyses of thiocyanate salts of lanthanides with hexamethylenetetramine in different hydration states.

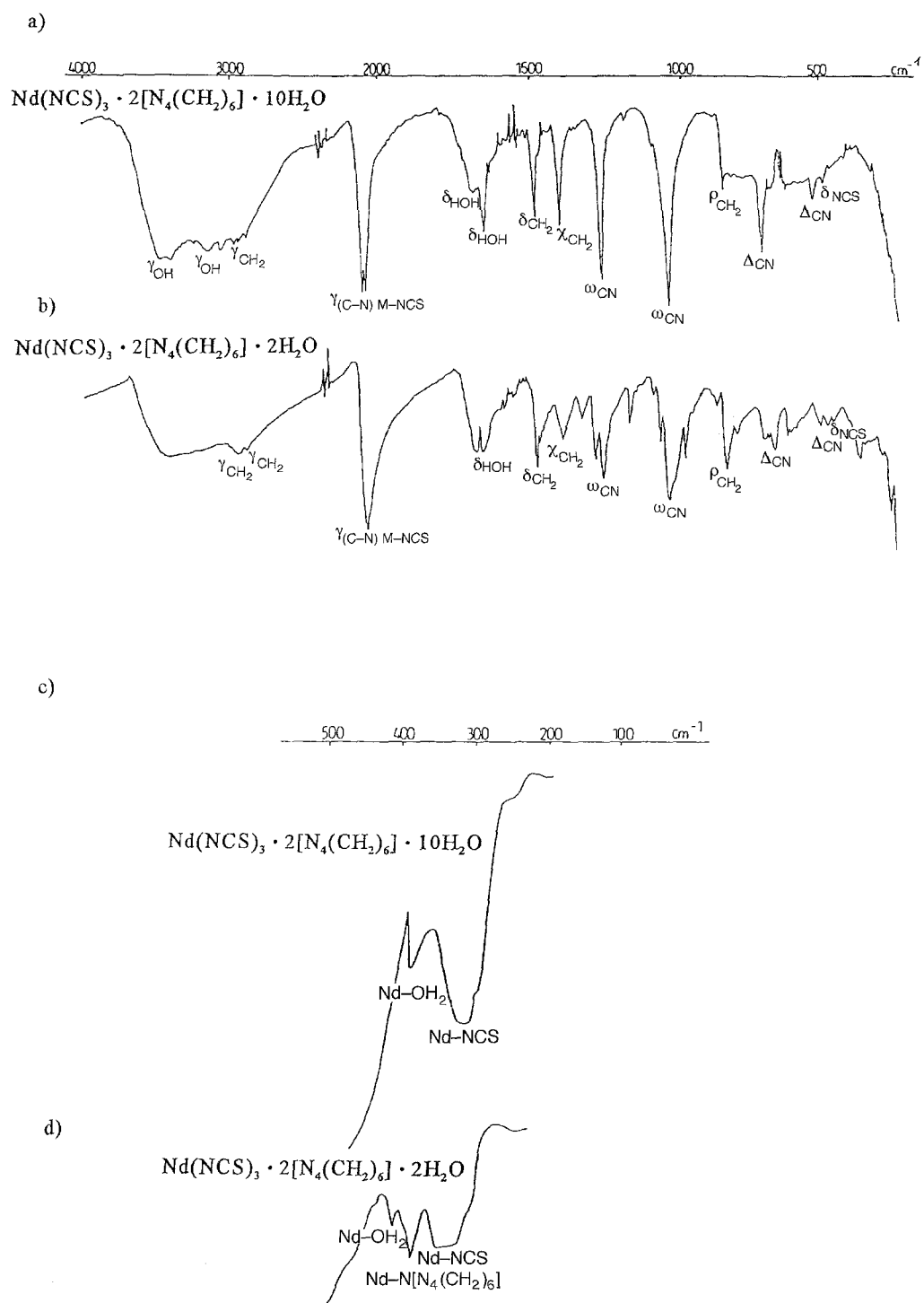
Spectroscopic examination indicates that at higher hydration states, the coordination sphere includes  $H_2O$  and  $NCS^-$ , whereas hexamethylenetetramine as well as some water molecules and  $NCS^-$  ions are outside the coordination sphere.

Structural studies of  $\text{La}(\text{NCS})_3 \cdot 2[\text{N}_4(\text{CH}_2)_6] \cdot 9\text{H}_2\text{O}$  fully confirmed the results of the IR analysis and allowed to determine the coordination number of lanthanum in the salt (9) as well as the number of  $\text{H}_2\text{O}$  molecules (7) and  $\text{NCS}^-$  ions = (2) bound to lanthanum [1]. In salts of lower hydration state the coordination sphere includes hexamethylenetetramine molecules,  $\text{H}_2\text{O}$  molecules, and  $\text{NCS}^-$  ions.

On the basis of the obtained diffraction patterns it was found that 9-hydrous lanthanum and praseodymium salts and 10-hydrous neodymium salt are isostructural. From the values of magnetic moments determined by *Gouy's* method for 2-, 4-, 6-, 8-, and 10-hydrous neodymium salts, a linear correlation between  $1/\chi$  and  $T$  could be established. Slight differences were found in the determined magnetic susceptibility of these compounds.

**Table 1.** Assignment of bands in the IR spectra of  $\text{Gd}(\text{NCS})_3 \cdot 2[\text{N}_4(\text{CH}_2)_6] \cdot 8\text{H}_2\text{O}$  and  $\text{Gd}(\text{NCS})_3 \cdot 2[\text{N}_4(\text{CH}_2)_6] \cdot 2\text{H}_2\text{O}$ ;  $\Delta$ : valency CN vibrations;  $\omega$ : deformation CN vibrations;  $\delta$ : deformation vibrations;  $\nu$ : stretching vibrations;  $\rho$ : fan vibrations;  $\kappa$ : swinging vibrations

$\text{Gd}(\text{NCS})_3 \cdot 2[\text{N}_4(\text{CH}_2)_6] \cdot 8\text{H}_2\text{O}$		$\text{Gd}(\text{NCS})_3 \cdot 2[\text{N}_4(\text{CH}_2)_6] \cdot 2\text{H}_2\text{O}$	
$\nu \text{ cm}^{-1}$	Vibration	$\nu \text{ cm}^{-1}$	Vibration
470	$\delta_{\text{NCS}}$	472	$\delta_{\text{NCS}}$
490	$\delta_{\text{NCS}}$	500	$\delta_{\text{NCS}}$
510	$\Delta_{\text{CN}}$	520	$\Delta_{\text{CN}}$
610		600	
625		615	
660		650	
690	$\Delta_{\text{CN}}$	690	$\Delta_{\text{CN}}$
810	$\rho_{\text{CH}_2}$	780	$\nu_{(\text{C-S})\text{Ln-NCS}}$
1005	$\omega_{\text{CN}}$	815	$\rho_{\text{CH}_2}$
1235	$\omega_{\text{CN}}$	960	$\omega_{\text{CN}}$
1380	$\kappa_{\text{CH}_2}$	1010	$\omega_{\text{CN}}$
1450		1040	$\omega_{\text{CN}}$
1465	$\delta_{\text{CH}_2}$	1150	
		1235	$\omega_{\text{CN}}$
1630	$\delta_{\text{HOH}}$	1260	$\omega_{\text{CN}}$
1660	$\delta_{\text{HOH}}$	1310	$\omega_{\text{CN}}$
2040	$\nu_{1(\text{CN})\text{Ln-NCS}}$	1375	$\kappa_{\text{CH}_2}$
2060	$\nu_{1(\text{CN})\text{Ln-NCS}}$	1450	
		1460	$\delta_{\text{CH}_2}$
		1640	$\delta_{\text{HOH}}$
		1670	$\delta_{\text{HOH}}$
2600–3700	$\nu_{\text{CH}_2}, \nu_{\text{CH}_2}$	2060	$\nu_{(\text{CN})\text{Ln-NCS}}$
	$\nu_{\text{OH}}, \nu_{\text{asOH}}$	2880	$\nu_{\text{CH}_2}$
		2950	$\nu_{\text{CH}_2}$
		3000–3700	$\nu_{\text{OH}}, \nu_{\text{asOH}}$



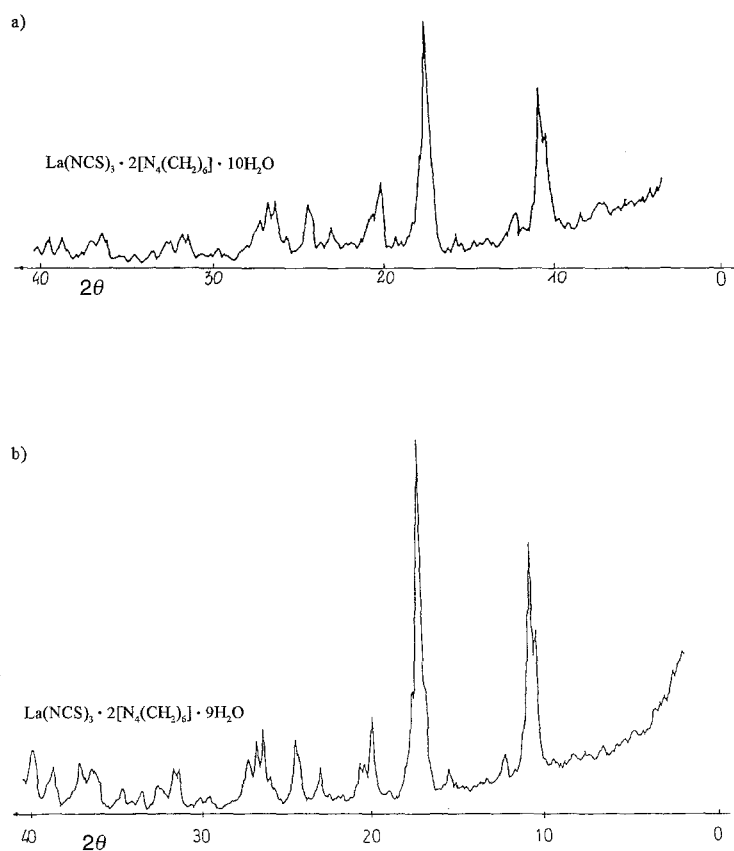
**Fig. 1.** IR spectra (400–4000  $\text{cm}^{-1}$ ) of a)  $\text{Nd}(\text{NCS})_3 \cdot 2[\text{N}_4(\text{CH}_2)_6] \cdot 10\text{H}_2\text{O}$ , b)  $\text{Nd}(\text{NCS})_3 \cdot 2[\text{N}_4(\text{CH}_2)_6] \cdot 2\text{H}_2\text{O}$ ; IR spectra (200–400  $\text{cm}^{-1}$ ) of c)  $\text{Nd}(\text{NCS})_3 \cdot 2[\text{N}_4(\text{CH}_2)_6] \cdot 10\text{H}_2\text{O}$ , d)  $\text{Nd}(\text{NCS})_3 \cdot 2[\text{N}_4(\text{CH}_2)_6] \cdot 2\text{H}_2\text{O}$

## Results and Discussion

### IR Spectroscopic Analysis

IR spectra were analyzed in the range of 200–4000  $\text{cm}^{-1}$  for the following salts:  $\text{La}(\text{NCS})_3 \cdot 2[\text{N}_4(\text{CH}_2)_6] \cdot 10\text{H}_2\text{O}$ ,  $\text{La}(\text{NCS})_3 \cdot 2[\text{N}_4(\text{CH}_2)_6] \cdot 9\text{H}_2\text{O}$ ,  $\text{La}(\text{NCS})_3 \cdot 2[\text{N}_4(\text{CH}_2)_6] \cdot 5\text{H}_2\text{O}$ ,  $\text{Pr}(\text{NCS})_3 \cdot 2[\text{N}_4(\text{CH}_2)_6] \cdot 9\text{H}_2\text{O}$ ,  $\text{Pr}(\text{NCS})_3 \cdot 2[\text{N}_4(\text{CH}_2)_6] \cdot 5\text{H}_2\text{O}$ ,  $\text{Nd}(\text{NCS})_3 \cdot 2[\text{N}_4(\text{CH}_2)_6] \cdot 10\text{H}_2\text{O}$ ,  $\text{Nd}(\text{NCS})_3 \cdot 2[\text{N}_4(\text{CH}_2)_6] \cdot 8\text{H}_2\text{O}$ ,  $\text{Nd}(\text{NCS})_3 \cdot 2[\text{N}_4(\text{CH}_2)_6] \cdot 6\text{H}_2\text{O}$ ,  $\text{Nd}(\text{NCS})_3 \cdot 2[\text{N}_4(\text{CH}_2)_6] \cdot 2\text{H}_2\text{O}$ ,  $\text{Sm}(\text{NCS})_3 \cdot 2[\text{N}_4(\text{CH}_2)_6] \cdot 10\text{H}_2\text{O}$ ,  $\text{Sm}(\text{NCS})_3 \cdot 2[\text{N}_4(\text{CH}_2)_6] \cdot 6\text{H}_2\text{O}$ ,  $\text{Gd}(\text{NCS})_3 \cdot 2[\text{N}_4(\text{CH}_2)_6] \cdot 8\text{H}_2\text{O}$ ,  $\text{Gd}(\text{NCS})_3 \cdot 2[\text{N}_4(\text{CH}_2)_6] \cdot 2\text{H}_2\text{O}$ ,  $\text{Dy}(\text{NCS})_3 \cdot 2[\text{N}_4(\text{CH}_2)_6] \cdot 5\text{H}_2\text{O}$ ,  $\text{Dy}(\text{NCS})_3 \cdot 2[\text{N}_4(\text{CH}_2)_6] \cdot \text{H}_2\text{O}$ , and  $\text{Er}(\text{NCS})_3 \cdot 2[\text{N}_4(\text{CH}_2)_6] \cdot 6\text{H}_2\text{O}$ .

Figure 1 presents the IR spectra of  $\text{Nd}(\text{NCS})_3 \cdot 2[\text{N}_4(\text{CH}_2)_6] \cdot 10\text{H}_2\text{O}$  and  $\text{Nd}(\text{NCS})_3 \cdot 2[\text{N}_4(\text{CH}_2)_6] \cdot \text{H}_2\text{O}$ . Table 1 lists vibration frequencies and the attributed types of vibrations of the salts  $\text{Gd}(\text{NCS})_3 \cdot 2[\text{N}_4(\text{CH}_2)_6] \cdot 8\text{H}_2\text{O}$  and  $\text{Gd}(\text{NCS})_3 \cdot 2[\text{N}_4(\text{CH}_2)_6] \cdot 2\text{H}_2\text{O}$ . Specific results of an IR analysis of  $\text{La}(\text{NCS})_3 \cdot 2[\text{N}_4(\text{CH}_2)_6] \cdot 9\text{H}_2\text{O}$  and the structure of this salt have been presented previously [1]. In Ref. [5], vibrations frequencies of  $\text{Nd}(\text{NCS})_3 \cdot 2[\text{N}_4(\text{CH}_2)_6] \cdot 10\text{H}_2\text{O}$  (50–500  $\text{cm}^{-1}$ ) are given.



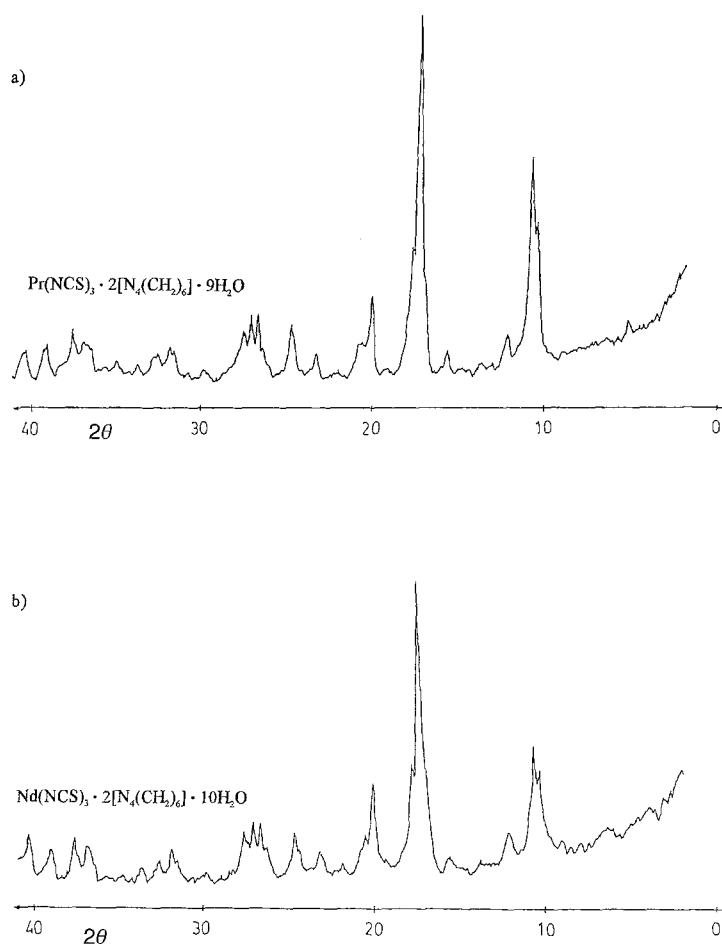
**Fig. 2.** X-ray diffraction pattern of a)  $\text{La}(\text{NCS})_3 \cdot 2[\text{N}_4(\text{CH}_2)_6] \cdot 10\text{H}_2\text{O}$ , b)  $\text{La}(\text{NCS})_3 \cdot 2[\text{N}_4(\text{CH}_2)_6] \cdot 9\text{H}_2\text{O}$

### *Diffraction Analysis*

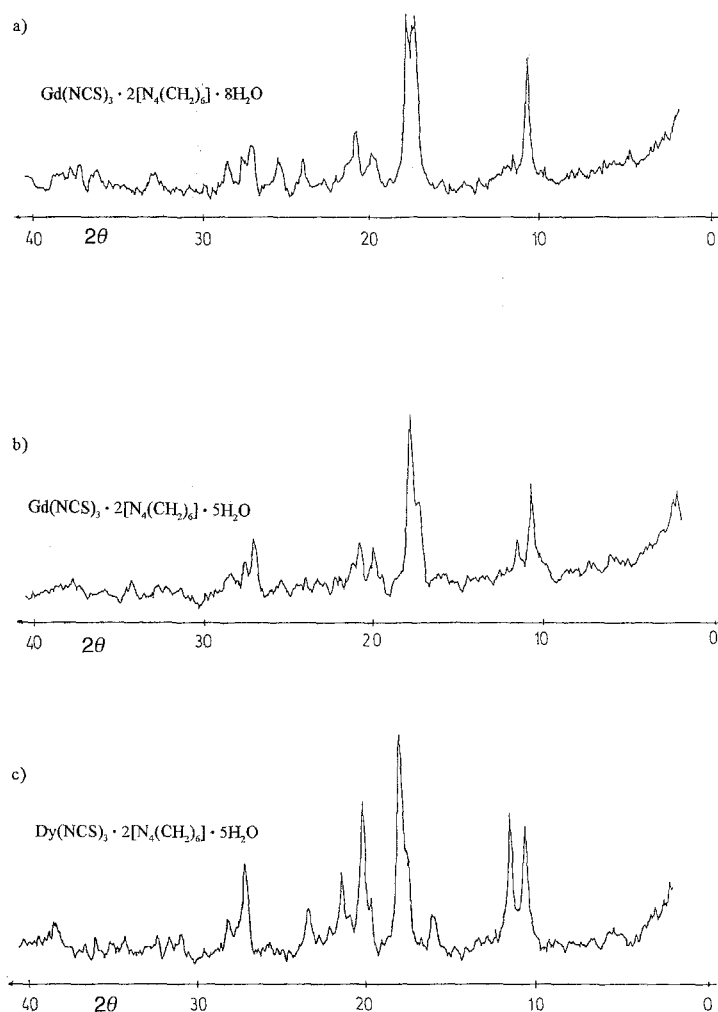
Diffraction patterns of the following compounds were obtained by the method of powder diffractometry:  $\text{La}(\text{NCS})_3 \cdot 2[\text{N}_4(\text{CH}_2)_6] \cdot 10\text{H}_2\text{O}$ ,  $\text{La}(\text{NCS})_3 \cdot 2[\text{N}_4(\text{CH}_2)_6] \cdot 9\text{H}_2\text{O}$ ,  $\text{Pr}(\text{NCS})_3 \cdot 2[\text{N}_4(\text{CH}_2)_6] \cdot 9\text{H}_2\text{O}$ ,  $\text{Nd}(\text{NCS})_3 \cdot 2[\text{N}_4(\text{CH}_2)_6] \cdot 10\text{H}_2\text{O}$ ,  $\text{Gd}(\text{NCS})_3 \cdot 2[\text{N}_4(\text{CH}_2)_6] \cdot 8\text{H}_2\text{O}$ ,  $\text{Gd}(\text{NCS})_3 \cdot 2[\text{N}_4(\text{CH}_2)_6] \cdot 5\text{H}_2\text{O}$ ,  $\text{Dy}(\text{NCS})_3 \cdot 2[\text{N}_4(\text{CH}_2)_6] \cdot 5\text{H}_2\text{O}$ . Figs. 2–4 show the diffraction patterns of these salts.

### *Analysis of Magnetic Susceptibility*

The values of magnetic susceptibility were determined by *Gouy's* method for neodymium salts with hexamethylenetetramine of different hydration states ( $n = 10, 8, 6, 4, 2$ ) and for the 6-hydrated samarium salt. The measurements were



**Fig. 3.** X-ray diffraction patterns of a)  $\text{Pr}(\text{NCS})_3 \cdot 2[\text{N}_4(\text{CH}_2)_6] \cdot 9\text{H}_2\text{O}$ , b)  $\text{Nd}(\text{NCS})_3 \cdot 2[\text{N}_4(\text{CH}_2)_6] \cdot 10\text{H}_2\text{O}$



**Fig. 4.** X-ray diffraction pattern of a)  $\text{Gd}(\text{NCS})_3 \cdot 2[\text{N}_4(\text{CH}_2)_6] \cdot 8\text{H}_2\text{O}$ , b)  $\text{Gd}(\text{NCS})_3 \cdot 2[\text{N}_4(\text{CH}_2)_6] \cdot 5\text{H}_2\text{O}$ , c)  $\text{Dy}(\text{NCS})_3 \cdot 2[\text{N}_4(\text{CH}_2)_6] \cdot 5\text{H}_2\text{O}$

performed in the temperature range of 77–300 K. Table 2 present the results for  $\text{Sm}(\text{NCS})_3 \cdot 2[\text{N}_4(\text{CH}_2)_6] \cdot 6\text{H}_2\text{O}$ .

Effective magnetic moments were determined on the basis of the following equation:

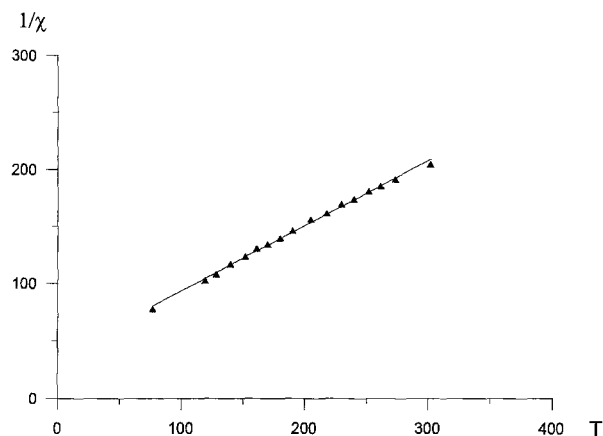
$$\mu_{\text{eff}} = 2.83 \sqrt{(\chi_g \cdot M - P)(T - \Theta)} \cdot MB$$

$\chi_g$ : gram-magnetic susceptibility,  $M$ : molar mass of the analyzed substance,  $T$ : temperature (K),  $\Theta$ : characteristic constant of the given substance,  $P$ : diamagnetic correction,  $MB$  – atomic unit of the magnetic moment (*Bohr magneton*). Figure 5 presents the dependence of the magnetic susceptibility  $\chi$  on the temperature for  $\text{Nd}(\text{NCS})_3 \cdot 2[\text{N}_4(\text{CH}_2)_6] \cdot 8\text{H}_2\text{O}$ .

**Table 2.** Results of magnetic study of  $\text{Sm}(\text{NCS})_3 \cdot 2[\text{N}_4(\text{CH}_2)_6] \cdot 6\text{H}_2\text{O}$ 

T(K)	$\chi_m$ (magnetic susceptibility exp.)	$\chi_{\text{calc}}$ (magnetic susceptibility calc.)	$\chi \cdot T$	$\mu_{\text{eff}}(\text{BM})$ $2.83 \cdot \sqrt{\chi_m \cdot T}$	$1/\chi_m$	$\mu_{\text{eff}}(\text{BM})$ $2.83 \cdot \sqrt{\chi_m(T - \Theta)}$
81	0.0012	0.00118	0.097	0.88	831.46	2.29
114	0.0012	0.00111	0.128	1.01	889.45	2.28
121	0.0011	0.0011	0.133	1.03	906.70	2.27
130	0.00108	0.00108	0.141	1.06	924.63	2.27
138	0.00106	0.00107	0.147	1.09	936.98	2.26
146	0.00105	0.00105	0.154	1.11	949.67	2.26
159	0.00103	0.00103	0.164	1.15	969.36	2.27
169	0.00101	0.00101	0.171	1.17	989.88	2.26
178	0.000995	0.001	0.177	1.19	1004.05	2.26
190	0.000981	0.000985	0.187	1.22	1018.63	2.27
200	0.000967	0.00097	0.193	1.24	1033.65	2.27
211	0.000953	0.000954	0.201	1.27	1049.11	2.27
221	0.000938	0.00094	0.208	1.29	1065.04	2.27
232	0.000924	0.000926	0.215	1.31	1081.46	2.27
242	0.00091	0.000912	0.220	1.33	1098.40	2.27
254	0.000896	0.000897	0.228	1.35	1115.87	2.27
265	0.000889	0.000884	0.236	1.37	1124.82	2.28
276	0.000874	0.000871	0.241	1.39	1143.16	2.28
292	0.00086	0.00085	0.251	1.42	1162.10	2.28

$\bar{\mu}_{\text{eff}} = 2.27$

**Fig. 5.** Dependence of invers magnetic susceptibiliy on the temperature for  $\text{Nd}(\text{NCS})_3 \cdot 2[\text{N}_4(\text{CH}_2)_6] \cdot 8\text{H}_2\text{O}$ 

## Conclusions

To interpret the IR spectra of the complex salts, it is necessary to consider free vibrations of hexamethylenetetramine [6], water [7, 8], and thiocyanate ions [9]. The IR spectra of lanthanide chloride salts with hexamethylenetetramine have been discussed in Ref. [10].

The analysis of the IR spectra shows differences between the vibration frequencies of salts of high and low hydration states. Thus, in the 10- to 6-hydrated salts, the shape and location of frequencies attributed to vibrations of CN and CH<sub>2</sub> of the hexamethylenetetramine ring indicate that the N<sub>4</sub>(CH<sub>2</sub>)<sub>6</sub> molecule does not belong to the coordination sphere of the lanthanides.

In the 5- to 1-hydrated salts, the vibrations are split into three parts, which implies a symmetry loss of N<sub>4</sub>(CH<sub>2</sub>)<sub>6</sub> and consequently indicates a bond between Ln and N<sub>4</sub>(CH<sub>2</sub>)<sub>6</sub>. The band of deformations  $\delta_{\text{HOH}}$  of the salts is also split, implying unequal bonds with the H<sub>2</sub>O molecule.

In the salts of high hydration state, a distinct broad band appears at frequencies of 2600–3700 cm<sup>-1</sup> which cannot, however, be explicitly interpreted. In the compounds with lower content of water, the bands split. Two bands can be observed corresponding to valence vibrations of N<sub>4</sub>(CH<sub>2</sub>)<sub>6</sub> ( $\nu_{\text{CH}_2}$  at 2880 cm<sup>-1</sup>,  $\nu_{\text{CH}}$  at 2950 cm<sup>-1</sup>). From 3000 to 3700 cm<sup>-1</sup>, a broad band appears which is attributed to valence vibrations  $\nu_{\text{sOH}}$  and  $\nu_{\text{asOH}}$ .

Thiocyanate ions can bind with metal through N or S atoms; alternatively, both atoms can be involved at the same time forming an Ln-NCS-Ln bridge. The formation of the bond with the metal does not change the symmetry of the anion; therefore, the coordination causes no splitting in the free vibrations of the anion. The bond between Ln and the thiocyanate anion causes a shift in the bands of vibrations  $\nu_{1(\text{CN})}$  and  $\nu_{3(\text{CS})}$  which may be connected with the type of the bond [9].

The IR spectra suggest that the thiocyanate ions and the hexamethylenetetramine molecules in these compounds may be bonded to the central ion *via* nitrogen [11–13]. Their analysis indicates a shift of the band of free vibration of NCS<sup>-</sup> and differences in its shape between salts of high and low hydration state. In the salts of high and low hydration state, the maxima of the  $\nu_{2(\text{NCS})}$  vibration bands occur at 470–490 cm<sup>-1</sup>. This location points to an Ln-NCS bond (Ln-SCN: 430–470 cm<sup>-1</sup>, Ln-NCS-Ln: 440–470 cm<sup>-1</sup>).  $\nu_{3(\text{CS})}$ , which can occur at 700–870 cm<sup>-1</sup>, is difficult to interpret as it is covered by the CH<sub>2</sub> vibrations of N<sub>4</sub>(CH<sub>2</sub>)<sub>6</sub>.

The  $\nu_{1(\text{CN})}$  vibration band of the NCS<sup>-</sup> ion the salts of high hydration state exhibits two maxima at 2040 and 2060 cm<sup>-1</sup>, whereas in the salts of low hydration state a single band at 2060 cm<sup>-1</sup> is observed. The location of this band indicates a Ln-NCS bond (according to Ref. [9], it appears at 2050–2100 cm<sup>-1</sup> for Ln-NCS, at 2085–2130 cm<sup>-1</sup> for Ln-SCN, and at 2065–2165 cm<sup>-1</sup> for Ln-NCS-Ln. The split of this band in salts of high hydration state implies that the NCS<sup>-</sup> bonds in these compounds are of different character. The Ln-NCS bond gives rise to vibrations in the far infrared; the band at 300 cm<sup>-1</sup> in the examined salts is attributed to this bond.

To sum up the results of the IR spectroscopic analysis, it should be stated that in salts of high hydration state, H<sub>2</sub>O molecules and NCS<sup>-</sup> ions belong to the coordination sphere of the lanthanides. N<sub>4</sub>(CH<sub>2</sub>)<sub>6</sub> molecules and other water molecules as well as NCS<sup>-</sup> ions are outside the coordination sphere of the lanthanides. In salts of low hydration state, N<sub>4</sub>(CH<sub>2</sub>)<sub>6</sub> and NCS<sup>-</sup> ions are in the coordination sphere. The way in which N<sub>4</sub>(CH<sub>2</sub>)<sub>6</sub> is bound depends on the state of hydration of the thiocyanate salt.

The X-ray structure determination of La(NCS)<sub>3</sub>·2[N<sub>4</sub>(CH<sub>2</sub>)<sub>6</sub>]·9H<sub>2</sub>O [1] proved that 2 NCS<sup>-</sup> ions and 7 water molecules are bound directly with lanthanum,



whereas  $\text{N}_4(\text{CH}_2)_6$ , NCS, and 2  $\text{H}_2\text{O}$  molecules are located at a longer distance from lanthanum. The coordination number of lanthanum is 9. On the basis of the obtained diffraction patterns, it was found that the 9-hydrous salt of lanthanum, the 10-hydrous salt of lanthanum, 9-hydrous salt of praseodymium, and the 10-hydrous neodymium salt are isostructural (Figs. 2–4).

Linear correlations of the inverse magnetic susceptibility ( $1/\chi$ ) upon temperature were found for Nd salts of different hydration state ( $n = 2, 4, 6, 8, 10$ ; Fig. 5). The compounds satisfy Curie's law. There are slight differences between the determined values of magnetic susceptibility of neodymium compounds of different hydration states.

## Experimental

### *Apparatus and reagents*

IR spectra in the range of  $200\text{--}400\text{ cm}^{-1}$  were recorded with a Perkin-Elmer spectrophotometer model 577, as nujol mull and in the range of  $400\text{--}4000\text{ cm}^{-1}$  with a Specord M-80 spectrophotometer as KBr pellets.

Diffractometric analysis was performed using a DRON-1 diffractometer with  $\text{Cu-K}\alpha$  radiation ( $\lambda = 1.5419\text{ \AA}$ ) and a nickel filter. The intensity of radiation was registered in the range of  $2\theta$  angles from  $2$  to  $80^\circ$ . Magnetic susceptibility was measured placing the sample in a capillary and putting it between the poles of an electromagnet, one end of the capillary in the magnetic field ( $H_{\text{max}}$ ) and the other one at vanishing magnetic field ( $H = 0$ ).

The change of mass at a given magnetic field was determined by means of Gouy's balance.  $\text{Hg}[\text{Co}(\text{NCS})_4]$  was applied as a standard substance (liquid nitrogen,  $77\text{ K}$ ). The temperature was measured with a platinum resistance thermometer in connection with a Wheatstone bridge MWH-91.

The following reagents were used for the syntheses: analytically pure hexamethylenetetramine (HMTA)  $\text{N}_4(\text{CH}_2)_6$  manufactured by P.O.Ch. Gliwice, 99.9% pure lanthanide oxides produced by Koch. Light. Lab. Fluka A.G., 96% ethanol, concentrated HCl, and KNCS manufactured by P.O.Ch. Gliwice. HNCS was purified by distillation [2].

### *Preparation methods*

Lanthanide salts with thiocyanates and hexamethylenetetramine were obtained in three ways: by dissolving lanthanide oxides in thiocyanic acid and then mixing with HMTA; by dissolving lanthanide oxides in hydrochloric acid (1 + 1) and exchange reaction by mixing lanthanide chlorides with saturated KNCS solution and then with HMTA solution; and by thermal dehydration.

### *Preparation of salts using thiocyanic acid*

Weighed samples of lanthanide oxides (1.62 g  $\text{La}_2\text{O}_3$ ; 1.70 g  $\text{Pr}_6\text{O}_{11}$ ; 1.68 g  $\text{Nd}_2\text{O}_3$ ; 1.74 g  $\text{Sm}_2\text{O}_3$ ; 1.81 g  $\text{Gd}_2\text{O}_3$ ; 1.66 g  $\text{Dy}_2\text{O}_3$ ; 1.91 g  $\text{Er}_2\text{O}_3$ ) were dissolved without heating in freshly prepared thiocyanic acid [2]. Thiocyanic acid was added in small portions under vigorous stirring. The obtained solutions were cooled and then mixed with a cooled saturated aqueous solutions containing 2.8 g of hexamethylenetetramine. When a precipitate appeared in the mixture, the samples were placed in a refrigerator for about 1 h. The precipitates were filtered off and dried on air at room temperature. This method yielded the lanthanum salts (white), neodymium salt (purple), gadolinium

salt (white), dysprosium salt (white), and erbium salt (light pink). The praseodymium salt does not precipitate under these conditions. The obtained salts were analyzed; their stoichiometric compositions are presented in Table 3.

#### Preparation of salts by exchange reactions

Weighed samples of lanthanide oxides (1.62 g  $\text{La}_2\text{O}_3$ ; 1.70 g  $\text{Pr}_6\text{O}_{11}$ ; 1.68 g  $\text{Nd}_2\text{O}_3$ ; 1.81 g  $\text{Gd}_2\text{O}_3$ ) were dissolved under heating in the smallest possible amount of hydrochloric acid (1 + 1) [3]. The cooled solutions were placed in a refrigerator. After about 12 h precipitates of hydrated lanthanide chlorides appeared. They were dissolved in 25 ml of 96% ethyl alcohol and added to hot alcoholic solution of potassium thiocyanate (2.9 g KNCS in 90 ml of 96% ethanol). The amount of potassium thiocyanate was such that the molar ratio of lanthanides to NCS was 1:3. The obtained solutions with precipitated KCl were refrigerated for about 12 h so that KCl could precipitate completely. Then the precipitate was separated from the solutions. The solutions of lanthanide thiocyanates were mixed with aqueous solutions of HMTA (2.8 g HMTA in 4 ml of water). Vigorous stirring caused a precipitate to form. The samples were kept in a refrigerator for about one hour; then the precipitates were filtered through salt filters and dried on air at room temperature (Table 4).

#### Preparation of salts by thermal dehydration

The salts of lower hydration state were obtained by heating hydrated salts in a drier up to temperatures determined from thermal curves. The salts were heated at the same rate at which they had been heated to obtain the thermal curves ( $2.5^\circ\text{C}/\text{min}$ ). Table 5 presents the results of the analyses of salts obtained by thermal dehydration. The temperatures at which individual salts were obtained and the mass losses determined from TG curves caused by dehydration in the course of the preparation of the salts and calculated from dehydration reactions are listed in Table 6.

**Table 3.** Analysis of salts prepared using thiocyanic acid ( $L = \text{N}_4(\text{CH}_2)_6$ )

	Melting temp. ( $^\circ\text{C}$ ) from DTA curve	%Ln Calc. Exp.	%NCS Calc. Exp.	%C Calc. Exp.	%N Calc. Exp.	%S Calc. Calc. Exp.	%H Calc. Exp.
$\text{La}(\text{NCS})_3 \cdot \text{L}_2 \cdot 10\text{H}_2\text{O}$	167.5	17.95	22.75	23.28	19.92	12.43	5.74
		17.78	22.35	23.19	20.30	11.69	5.76
$\text{Nd}(\text{NCS})_3 \cdot \text{L}_2 \cdot 10\text{H}_2\text{O}$	160.0	18.51	22.36	23.12	19.78	12.35	5.70
		18.50	22.62	24.72	20.43	11.14	5.71
$\text{Sm}(\text{NCS})_3 \cdot \text{L}_2 \cdot 10\text{H}_2\text{O}$	158.0	19.17	22.20	22.96	19.62	12.25	5.61
		19.02	22.11	23.01	19.98	11.55	5.69
$\text{Gd}(\text{NCS})_3 \cdot \text{L}_2 \cdot 5\text{H}_2\text{O}$	164.0	22.40	24.81	25.66	21.95	13.70	4.89
		22.74	24.89	25.86	21.91	12.75	5.00
$\text{Dy}(\text{NCS})_3 \cdot \text{L}_2 \cdot 5\text{H}_2\text{O}$	174.0	22.97	24.64	25.47	21.79	13.60	4.86
		22.89	24.22	25.82	21.24	12.80	5.05
$\text{Er}(\text{NCS})_3 \cdot \text{L}_2 \cdot 6\text{H}_2\text{O}$		22.90	23.67	24.98	21.11	13.17	4.98
		22.60	23.32	25.14	21.26	12.62	4.99

**Table 4.** Analysis of salts prepared by exchange reaction ( $L = N_4(CH_2)_6$ )

	Melting temp. (°C) from DTA curve	%Ln Calc. Exp.	%NCS Calc. Exp.	%C Calc. Exp.	%N Calc. Exp.	%S Calc. Calc. Exp.	%H Calc. Exp.
La(NCS) <sub>3</sub> ·L <sub>2</sub> ·9H <sub>2</sub> O	168	18.38	23.05	23.84	20.39	12.73	5.61
		18.41	22.45	24.65	19.98	12.61	5.82
Pr(NCS) <sub>3</sub> ·L <sub>2</sub> ·9H <sub>2</sub> O	163	18.59	22.99	23.77	20.34	12.69	5.60
		18.59	22.63	24.01	20.56	12.47	5.86
Nd(NCS) <sub>3</sub> ·L <sub>2</sub> ·8H <sub>2</sub> O	159	19.41	22.45	24.24	20.74	12.94	5.44
		19.27	21.71	24.48	20.43	12.39	5.65
Gd(NCS) <sub>3</sub> ·L <sub>2</sub> ·8H <sub>2</sub> O	164	20.64	23.04	23.83	20.38	12.72	5.34
		20.81	22.93	23.80	19.97	12.08	5.24

**Table 5.** Analysis of salts prepared by thermal dehydration ( $L = N_4(CH_2)_6$ )

	%Ln Calc. Exp.	%NCS Calc. Exp.	%C Calc. Exp.	%N Calc. Exp.	%S Calc. Calc. Exp.	%H Calc. Exp.
La(NCS) <sub>3</sub> ·L <sub>2</sub> ·H <sub>2</sub> O	20.59	25.82	26.70	22.84	13.71	4.94
	19.62	25.44	25.32	20.94	11.37	5.76
Pr(NCS) <sub>3</sub> ·L <sub>2</sub> ·5H <sub>2</sub> O <sup>1</sup>	20.55	25.41	26.25	22.46	14.03	5.91
	20.82	25.49	26.56	22.88	13.71	6.41
Pr(NCS) <sub>3</sub> ·L <sub>2</sub> ·2H <sub>2</sub> O <sup>1</sup>	22.31	27.54	28.50	22.42	15.14	4.48
	22.16	27.54	27.97	22.63	14.01	5.00
Nd(NCS) <sub>3</sub> ·L <sub>2</sub> ·6H <sub>2</sub> O	20.40	24.64	25.48	21.80	13.60	5.14
	20.35	23.91	25.96	22.01	13.26	5.47
Nd(NCS) <sub>3</sub> ·L <sub>2</sub> ·4H <sub>2</sub> O <sup>1</sup>	21.50	25.27	26.85	22.97	13.96	4.84
	20.70	24.52	26.78	22.31	13.55	5.19
Nd(NCS) <sub>3</sub> ·L <sub>2</sub> ·3H <sub>2</sub> O	22.09	26.68	27.59	23.60	14.73	4.64
	22.50	26.62	27.89	22.98	14.43	5.17
Nd(NCS) <sub>3</sub> ·L <sub>2</sub> ·2H <sub>2</sub> O <sup>1</sup>	22.72	27.44	28.37	24.27	15.15	4.45
	22.38	26.96	28.39	23.89	14.91	4.49
Sm(NCS) <sub>3</sub> ·L <sub>2</sub> ·6H <sub>2</sub> O	21.10	24.44	25.27	21.60	13.49	5.05
	20.85	24.01	26.02	21.84	12.98	5.00
Gd(NCS) <sub>3</sub> ·L <sub>2</sub> ·1,5H <sub>2</sub> O <sup>1</sup>	24.61	27.27	28.19	24.12	15.02	4.27
	24.57	27.07	27.95	23.70	14.46	4.70
Gd(NCS) <sub>3</sub> ·L <sub>2</sub> ·H <sub>2</sub> O	24.96	27.65	28.60	24.46	15.27	4.17
	24.75	27.19	27.93	24.27	14.58	4.27
Dy(NCS) <sub>3</sub> ·L <sub>2</sub> ·H <sub>2</sub> O	25.58	27.43	28.37	24.26	15.14	4.13
	25.78	27.32	28.22	23.94	14.46	4.32

<sup>1</sup> Salts prepared by thermal dehydration of compounds obtained by exchange reaction

**Table 6.** Temperatures for preparation of salts by thermal dehydration ( $L = \text{N}_4(\text{CH}_2)_6$ )

	Temperature of decomposition ( $^{\circ}\text{C}$ )	Compound obtained by thermal dehydration
$\text{La}(\text{NCS})_3 \cdot \text{L}_2 \cdot 9\text{H}_2\text{O}$	105	$\text{La}(\text{NCS})_3 \cdot \text{L}_2 \cdot 8\text{H}_2\text{O}$
$\text{Pr}(\text{NCS})_3 \cdot \text{L}_2 \cdot 9\text{H}_2\text{O}$	10 125	$\text{Pr}(\text{NCS})_3 \cdot \text{L}_2 \cdot 5\text{H}_2\text{O}$ $\text{Pr}(\text{NCS})_3 \cdot \text{L}_2 \cdot 2\text{H}_2\text{O}$
$\text{Nd}(\text{NCS})_3 \cdot \text{L}_2 \cdot 10\text{H}_2\text{O}$	86 120	$\text{Nd}(\text{NCS})_3 \cdot \text{L}_2 \cdot 6\text{H}_2\text{O}$ $\text{Nd}(\text{NCS})_3 \cdot \text{L}_2 \cdot 3\text{H}_2\text{O}$
$\text{Nd}(\text{NCS})_3 \cdot \text{L}_2 \cdot 8\text{H}_2\text{O}$	96 112	$\text{Nd}(\text{NCS})_3 \cdot \text{L}_2 \cdot 4\text{H}_2\text{O}$ $\text{Nd}(\text{NCS})_3 \cdot \text{L}_2 \cdot 2\text{H}_2\text{O}$
$\text{Sm}(\text{NCS})_3 \cdot \text{L}_2 \cdot 10\text{H}_2\text{O}$	90 120	$\text{Sm}(\text{NCS})_3 \cdot \text{L}_2 \cdot 6\text{H}_2\text{O}$ $\text{Sm}(\text{NCS})_3 \cdot \text{L}_2 \cdot 2\text{H}_2\text{O}$
$\text{Gd}(\text{NCS})_3 \cdot \text{L}_2 \cdot 8\text{H}_2\text{O}$	125	$\text{Gd}(\text{NCS})_3 \cdot \text{L}_2 \cdot 1.5\text{H}_2\text{O}$
$\text{Gd}(\text{NCS})_3 \cdot \text{L}_2 \cdot 5\text{H}_2\text{O}$	125	$\text{Gd}(\text{NCS})_3 \cdot \text{L}_2 \cdot \text{H}_2\text{O}$
$\text{Dy}(\text{NCS})_3 \cdot \text{L}_2 \cdot 5\text{H}_2\text{O}$	140	$\text{Dy}(\text{NCS})_3 \cdot \text{L}_2 \cdot \text{H}_2\text{O}$
$\text{Er}(\text{NCS})_3 \cdot \text{L}_2 \cdot 6\text{H}_2\text{O}$	120	$\text{Er}(\text{NCS})_3 \cdot \text{L}_2 \cdot 2\text{H}_2\text{O}$

*Chemical analysis*

The chemical analysis of the obtained salts included: determination of lanthanides by complexometric titration against xylenol orange [4] and determination of thiocyanates by *Volhard's* method; Nitrogen, carbon, hydrogen, and sulfur: elementary analysis; content of water: TG curves.

**Acknowledgements**

The author wishes to thank Professor *Jerzy Mroziński* for magnetic experiments.

**References**

- [1] Zalewicz M, Goliński B (in press); *commun.* (1992) 29<sup>th</sup> ICCS, Lausanne, Switzerland, P 762
- [2] Glund W, Keller K, Klempt W (1926) *Ber* **59**: 1384
- [3] Ferraro IR, Davis KC (1969) *Inorg Chim Acta* **3**: 685
- [4] Busiew AI, Tipcowa WG, Iwanow WM (1982) *Analytical Chemistry of Rare Earth Elements*. WNT, Warszawa
- [5] Zalewicz M, Oczko G, Legendziewicz J (1995) *J Appl Spectr* **62**, **4**: 114
- [6] Matieu I (1951) *J Chim Phys* **48**: 1; (1956) **53**: 106
- [7] Lucchesi PJ, Glasson WA (1956) *J Am Chem Soc* **78**: 1347
- [8] Hakagawa I, Shimanouchi T (1964) *Spectrochim Acta* **29**: 429
- [9] Kabesowa M, Gazo J (1980) *Chem Zvesti* **34**: 800
- [10] Zalewicz M (1990) *Monatsh Chem* **121**: 249
- [11] Bailey RA, Kozak SL, Michelsen TW, Mills WN (1971) *Coord Chem Rev* **6**: 407
- [12] Hart FA, Laming FP (1964) *J Inorg Nucl Chem* **26**: 579; (1965) **27**: 1825
- [13] Levis J, Nyholm R, Williams PJ (1961) *J Chem Soc*: 4590

*Received November 2, 1996. Accepted November 29, 1996*