

## Coordination Compounds of 2,6-Diacetylpyridinedihydrazone. Part 1. Preparation and Characterization of the Complexes with Lighter Lanthanide Chlorides, Perchlorates and Nitrates<sup>†</sup>

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(Received April 21, 1987)

### Abstract

The La, Ce, Pr, Nd, Sm, Eu and Gd complexes of 2,6-diacetylpyridinedihydrazone (L) with chlorides, perchlorates and nitrates as counterions have been prepared. They are formulated as  $[\text{LaL}(\text{H}_2\text{O})_6]\text{X}_3$ ,  $[\text{LnL}_2(\text{H}_2\text{O})_3]\text{X}_3 \cdot \text{H}_2\text{O}$  (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd and X =  $\text{Cl}^-$  or  $\text{ClO}_4^-$ ),  $[\text{LnL}_2(\text{NO}_3)_3] \cdot 2\text{H}_2\text{O}$  (Ln = La, Ce, Pr, Nd) and  $[\text{LnL}_2(\text{NO}_3)_3(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$  (Ln = Sm, Eu, Gd) on the basis of UV-Vis, IR and NMR spectroscopic data and thermal and elemental analysis. The correlation of the nature of metal, the type of counterion and preparative conditions with the stoichiometry and coordination mode in the complexes is discussed.

### Introduction

Interest in the study of hydrazones has been growing because of their physiological activity, coordinative capability and application in analytical chemistry [1, 2].

Although the hydrazone complexes of various transition metals have been studied [3–9] no work, to our knowledge, has been published on the coordinating ability of hydrazone ligands with the C=N–NH<sub>2</sub> moiety towards the lanthanides.

As a continuation of our systematic investigation of the macrocyclic and acyclic complexes formed in the reaction of the lanthanides with 2,6-diacetylpyridine and various amines, we have examined the chelating behaviour of 2,6-diacetylpyridinedihydrazone towards the lanthanides and the correlation of the type of counterion and the preparative conditions with the stoichiometry and the filling of the coordination sphere of the complexes.

The present paper deals with the synthesis and characterization of the La(III), Ce(III), Pr(III), Nd(III), Sm(III), Eu(III) and Gd(III) hydrazone

complexes with chlorides, perchlorates and nitrates as counterions. The coordinating properties of the title ligand towards the heavier lanthanides (Tb to Lu) will be discussed in a subsequent paper [10].

### Experimental

The hydrated lanthanide chlorides, perchlorates and nitrates were obtained from the oxides and appropriate acids in the usual way for the preparation of lanthanide salts [11].

#### Preparation of the 2,6-Diacetylpyridinedihydrazone (L)

2,6-Diacetylpyridine (0.06 mol) was dissolved in absolute ethanol (150 ml) and this solution was added dropwise to a stirred solution of hydrazine hydrate (0.3 mol) kept at 5 °C. After 8 h stirring at room temperature, the crude white product was filtered off, washed with ethanol and crystallized from ethyl acetate. Yield 85%. Melting point 181–182 °C. *Anal.* Found: C, 56.53; H, 6.81; N, 36.68. C<sub>9</sub>H<sub>13</sub>N<sub>5</sub> requires: C, 56.50; H, 6.85; N, 36.64%. The <sup>1</sup>H NMR (DMSO-d<sub>6</sub>) spectrum shows signals at δ 7.82, 6.79 and 2.25, assigned to the pyridine protons, NH<sub>2</sub> protons and methyl protons, respectively. The integrations of the signals were in the ratio 3:4:6.

#### Preparation of La, Ce, Pr, Nd, Sm, Eu and Gd Complexes of L: General Procedure

The mixture of appropriate lanthanide salt in ethanol and L in ethanol in the metal:ligand ratio 1:1, 1:2, 1:3 or 1:4 was refluxed for about 3 h. The precipitated yellow complexes were filtered, washed with ether and dried over P<sub>2</sub>O<sub>5</sub>. For the lanthanum chloride and perchlorate two type complexes with stoichiometry metal:hydrazone equal to 1:1 and 1:2 were isolated, depending upon the molar ratio of the metal ion and ligand used in the synthesis. The lanthanum nitrate and Ce, Pr, Nd, Sm, Eu and Gd chlorides, perchlorates and nitrates yield only 1:2 complexes with hydrazone irrespective of the molar ratios of the starting materials.

Table I reports the analytical data of the complexes.

<sup>†</sup>Presented in part at the XXIV International Conference on Coordination Chemistry, Athens, Greece, August 24–29, 1986.

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TABLE I. Analytical Data for the Lanthanide Complexes of 2,6-Diacetylpyridinedihydrazone (L)

Complex	Calculated (%)			Found (%)		
	C	H	N	C	H	N
[LaL(H <sub>2</sub> O) <sub>6</sub> ]Cl <sub>3</sub>	19.84	4.62	12.86	19.77	4.66	12.74
[LaL(H <sub>2</sub> O) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	14.68	3.42	9.51	14.68	3.44	9.60
[LaL <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub> ]Cl <sub>3</sub> ·H <sub>2</sub> O	30.89	4.90	20.01	31.06	4.92	20.09
[LaL <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>3</sub> ·H <sub>2</sub> O	24.24	3.84	15.71	24.34	3.87	15.76
[LaL <sub>2</sub> (NO <sub>3</sub> ) <sub>3</sub> ]·2H <sub>2</sub> O	29.08	4.07	24.49	29.37	4.02	24.40
[CeL <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub> ]Cl <sub>3</sub> ·H <sub>2</sub> O	30.84	4.89	19.98	30.68	4.87	19.91
[CeL <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>3</sub> ·H <sub>2</sub> O	24.21	3.84	15.68	24.09	3.79	15.55
[CeL <sub>2</sub> (NO <sub>3</sub> ) <sub>3</sub> ]·2H <sub>2</sub> O	29.03	4.06	24.45	28.89	4.04	24.39
[PrL <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>3</sub> ·H <sub>2</sub> O	24.19	3.83	15.67	24.12	3.78	15.61
[PrL <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub> ]Cl <sub>3</sub> ·H <sub>2</sub> O	30.80	4.88	19.96	30.71	4.87	19.92
[PrL <sub>2</sub> (NO <sub>3</sub> ) <sub>3</sub> ]·2H <sub>2</sub> O	29.00	4.06	24.43	28.84	4.05	24.48
[NdL <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub> ]Cl <sub>3</sub> ·H <sub>2</sub> O	30.66	4.86	19.86	30.75	4.92	19.95
[NdL <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>3</sub> ·H <sub>2</sub> O	24.10	3.82	15.61	23.99	3.85	15.49
[NdL <sub>2</sub> (NO <sub>3</sub> ) <sub>3</sub> ]·2H <sub>2</sub> O	28.87	4.04	24.32	28.76	4.06	24.27
[SmL <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub> ]Cl <sub>3</sub> ·H <sub>2</sub> O	30.40	4.82	19.69	29.91	4.78	19.56
[SmL <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>3</sub> ·H <sub>2</sub> O	23.94	3.79	15.51	23.87	3.77	15.47
[SmL <sub>2</sub> (NO <sub>3</sub> ) <sub>3</sub> (H <sub>2</sub> O)]·2H <sub>2</sub> O	27.79	4.17	23.56	28.09	4.20	23.39
[EuL <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub> ]Cl <sub>3</sub> ·H <sub>2</sub> O	30.33	4.81	19.65	30.19	4.79	19.56
[EuL <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>3</sub> ·H <sub>2</sub> O	23.89	3.78	15.48	23.99	3.81	15.59
[EuL <sub>2</sub> (NO <sub>3</sub> ) <sub>3</sub> (H <sub>2</sub> O)]·2H <sub>2</sub> O	27.91	4.16	23.51	27.71	4.21	23.62
[GdL <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub> ]Cl <sub>3</sub> ·H <sub>2</sub> O	30.10	4.77	19.50	30.23	4.82	19.59
[GdL <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>3</sub> ·H <sub>2</sub> O	23.75	3.77	15.39	23.59	3.75	15.27
[GdL <sub>2</sub> (NO <sub>3</sub> ) <sub>3</sub> (H <sub>2</sub> O)]·2H <sub>2</sub> O	27.73	4.14	23.35	27.54	4.16	23.29

### Measurements

The infrared spectra were recorded using CsI pellets in the range 4000–200 cm<sup>-1</sup> on a Perkin-Elmer 580 infrared spectrophotometer. The electronic spectra were measured on a Beckman 25 spectrophotometer. The nuclear magnetic resonance spectra were run on a Varian EM-360 60 MHz spectrometer for solutions in DMSO-d<sub>6</sub> using TMS as internal standard. Thermogravimetric measurements were performed using the Derivatograph OD-102, MOM.

### Results and Discussion

The trivalent La, Ce, Pr, Nd, Sm, Eu and Gd complexes of 2,6-diacetylpyridinedihydrazone were prepared by direct reaction of the metal chloride, perchlorate and nitrate salts with ligand in ethanol and were identified by spectral data (IR, UV-Vis, NMR) and thermal and elemental analysis. The complexes are yellow, air-stable solids, appreciably soluble in DMSO and slightly soluble in acetonitrile.

The infrared spectra in the region 4000–200 cm<sup>-1</sup> provide some information regarding the mode of coordination in the complexes and were analysed in comparison with that of the free ligand. The most relevant bands and proposed assignments for the free ligand and the complexes are listed in Tables II and III.

All the spectra are very similar to one another except for the anion and water vibrational modes, but they are different from spectra of the free ligand. The most significant variations between free ligand and complexes concern the  $\nu(\text{C}=\text{N})$ ,  $\nu(\text{N}-\text{N})$  and pyridine ring bands.

The medium band at 1600 cm<sup>-1</sup> in the free ligand attributable to  $\nu(\text{C}=\text{N})$  stretching vibrations is shifted by 45–60 cm<sup>-1</sup> upon complexation to lower frequencies, as expected from reducing the electron density on the nitrogen atom because of coordination with lanthanide(III) cations. The N–N frequency found at 1150 cm<sup>-1</sup> in the free ligand increases by 45–60 cm<sup>-1</sup> in the complexes, suggesting the involvement of one of the nitrogen atoms in the bonding with the metal ion, which causes a reduction in electron repulsion by the lone pairs on adjacent nitrogen atoms [12]. The non-bonding of the NH<sub>2</sub> nitrogen atom is confirmed by the persistence of the  $\delta\text{NH}_2$  vibration occurring at 1635 cm<sup>-1</sup> in the free ligand and complexes, and the shifting of anti-symmetric and symmetric stretching vibrations of NH<sub>2</sub> groups from 3360 and 3200 cm<sup>-1</sup> for the free ligand towards the higher frequency region in metal complexes.

Evidence for the coordination of the pyridine nitrogen atom comes from systematic shifts to higher frequencies of bands characteristic of the pyridine ring vibrations [11]. The highest energy pyridine

TABLE II. Infrared (cm<sup>-1</sup>) and Electronic (nm) Spectral Data for 2,6-Diacetylpyridinedihydrazone (L) and its Complexes with Lanthanide Chlorides and Perchlorates

Compound	OH	NH <sub>2</sub>	C=N	py	N-N	ClO <sub>4</sub> <sup>-</sup>	M-N	λ
L		3360, 3200, 1635	1600	1570, 950, 640, 400	1150			275
[LaL(H <sub>2</sub> O) <sub>6</sub> ]Cl <sub>3</sub>	3500, 870	3400, 3295, 3195, 1635	1555	1590, 1000, 670, 420	1195		365	285, 358
[LaL(H <sub>2</sub> O) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	3500, 850	3420, 3305, 3200, 1635	1555	1590, 990, 655, 420	1200	1100, 620	360	278, 350
[LaL <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub> ]Cl <sub>3</sub> ·H <sub>2</sub> O	3540, 870	3400, 3295, 3190, 1633	1540	1590, 998, 670, 428	1200		370	282, 358
[LaL <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>3</sub> ·H <sub>2</sub> O	3530, 850	3410, 3295, 3200, 1635	1555	1595, 1000, 660, 430	1200	1100, 625	365	280, 350
[CeL <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub> ]Cl <sub>3</sub> ·H <sub>2</sub> O	3545, 865	3405, 3300, 3190, 1633	1540	1593, 998, 665, 430	1200		360	280, 358
[CeL <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>3</sub> ·H <sub>2</sub> O	3540, 850	3385, 3300, 3200, 1635	1550	1595, 995, 665, 430	1200	1095, 620	365	281, 352
[PrL <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub> ]Cl <sub>3</sub> ·H <sub>2</sub> O	3540, 860	3400, 3295, 3190, 1633	1540	1590, 1000, 670, 428	1200		370	283, 358
[PrL <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>3</sub> ·H <sub>2</sub> O	3540, 850	3390, 3300, 3200, 1635	1555	1595, 1000, 670, 435	1205	1095, 620	365	280, 352
[NdL <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub> ]Cl <sub>3</sub> ·H <sub>2</sub> O	3530, 850	3403, 3290, 3190, 1633	1543	1593, 1000, 672, 430	1200		370	283, 358
[NdL <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>3</sub> ·H <sub>2</sub> O	3530, 860	3400, 3295, 3205, 1635	1550	1598, 1003, 670, 430	1205	1098, 623	365	282, 353
[SmL <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub> ]Cl <sub>3</sub> ·H <sub>2</sub> O	3550, 855	3400, 3300, 3200, 1638	1543	1592, 1002, 673, 440	1205		373	285, 359
[SmL <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>3</sub> ·H <sub>2</sub> O	3540, 860	3410, 3295, 3205, 1638	1545	1598, 1005, 670, 440	1205	1100, 625	365	284, 355
[EuL <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub> ]Cl <sub>3</sub> ·H <sub>2</sub> O	3540, 850	3400, 3330, 3200, 1633	1548	1595, 1000, 670, 443	1202		375	287, 360
[EuL <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>3</sub> ·H <sub>2</sub> O	3540, 860	3410, 3300, 3205, 1638	1545	1595, 1005, 675, 440	1205	1100, 625	365	286, 357
[GdL <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub> ]Cl <sub>3</sub> ·H <sub>2</sub> O	3560, 900	3390, 3300, 3210, 1638	1545	1590, 1000, 670, 440	1205		385	287, 360
[GdL <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>3</sub> ·H <sub>2</sub> O	3550, 865	3420, 3290, 3205, 1638	1545	1598, 1005, 675, 440	1205	1100, 625	365	286, 357

TABLE III. Infrared (cm<sup>-1</sup>) and Electronic (nm) Spectral Data for 2,6-Diacetylpyridinedihydrazone (L) Complexes of Lanthanide Nitrates

Complex	OH	NH <sub>2</sub>	C=N	py	N-N	NO <sub>3</sub> <sup>-</sup>	M-N	λ
[LaL <sub>2</sub> (NO <sub>3</sub> ) <sub>3</sub> ]·2H <sub>2</sub> O	3550	3420, 3310, 3260, 1638	1547	1590, 1000, 655, 430	1200	1780, 1740, 1475, 1295, 1043, 815	348	280, 350
[CeL <sub>2</sub> (NO <sub>3</sub> ) <sub>3</sub> ]·2H <sub>2</sub> O	3560	3410, 3315, 3260, 1635	1548	1590, 998, 652, 430	1200	1780, 1740, 1480, 1295, 1045, 815	350	279, 350
[PrL <sub>2</sub> (NO <sub>3</sub> ) <sub>3</sub> ]·2H <sub>2</sub> O	3560	3400, 3320, 3260, 1638	1553	1598, 1000, 648, 430	1200	1780, 1735, 1475, 1290, 1045, 815	345	277, 347
[NdL <sub>2</sub> (NO <sub>3</sub> ) <sub>3</sub> ]·2H <sub>2</sub> O	3540	3420, 3320, 3240, 1638	1548	1590, 1005, 650, 435	1205	1775, 1735, 1480, 1300, 1035, 815	350	275, 347
[SmL <sub>2</sub> (NO <sub>3</sub> ) <sub>3</sub> (H <sub>2</sub> O)]·2H <sub>2</sub> O	3560, 850	3420, 3375, 3320, 3240, 1635	1552	1595, 1005, 652, 425	1205	1765, 1740, 1460, 1305, 1030, 818	350	276, 348
[EuL <sub>2</sub> (NO <sub>3</sub> ) <sub>3</sub> (H <sub>2</sub> O)]·2H <sub>2</sub> O	3560, 850	3420, 3375, 3320, 3250, 1635	1550	1597, 1005, 650, 425	1210	1765, 1745, 1455, 1310, 1035, 818	350	277, 346
[GdL <sub>2</sub> (NO <sub>3</sub> ) <sub>3</sub> (H <sub>2</sub> O)]·2H <sub>2</sub> O	3560, 848	3420, 3375, 3315, 3240, 1635	1552	1597, 1010, 655, 430	1210	1765, 1740, 1455, 1310, 1035, 818	350	277, 347

band observed in the spectrum of the ligand at  $1570\text{ cm}^{-1}$ , which corresponds to  $\nu(\text{C}=\text{N})$  of the heterocyclic ring, is shifted by about  $25\text{ cm}^{-1}$  to higher frequencies in the spectra of the complexes, indicating that the double bond character of  $\text{C}=\text{N}$  increases as a consequence of coordination by nitrogen. The bonding of the pyridine ring in the complexes is also shown by an increase of about  $50\text{ cm}^{-1}$  in the ring breathing frequency found at  $950\text{ cm}^{-1}$  in the spectrum of the free ligand. The low energy pyridine ring in-plane and out-of-plane vibrations also shift to higher frequencies, which is a good indication of coordination of the heterocyclic nitrogen.

The infrared spectra of the metal chloride and perchlorate complexes (Table II) do not show absorption bands characteristic of coordinated anions. The presence of uncoordinated perchlorates is inferred from the broad band centered at  $1100\text{ cm}^{-1}$  and the sharp medium band at *ca.*  $620\text{ cm}^{-1}$  observed for all perchlorate complexes.

The infrared spectra of all nitrate complexes (Table III) demonstrate the presence of coordinated anions. The bands at  $1390$  and  $830\text{ cm}^{-1}$  characteristic of ionic nitrate do not appear. The distinction between monodentate and bidentate nitrate groups may be established from the range of splitting and the magnitude of separation of the vibrational modes, which is indicative of the interaction strength between the metal and the oxygen atoms of the nitrates [13–15].

In the La, Ce, Pr, and Nd nitrate complexes of 2,6-diacetylpyridinedihydrazone, the two bands associated with the asymmetric stretch appear near  $1475$  and  $1295\text{ cm}^{-1}$ . The magnitude of the separation is about  $180\text{ cm}^{-1}$  and typical of bidentate bonding of nitrates. The separation of the combination frequencies in the  $1800$ – $1700\text{ cm}^{-1}$  region, which is commonly used to differentiate between bidentate and monodentate coordination of nitrates, is about  $40\text{ cm}^{-1}$  and consistent with the presence of bidentate nitrate groups.

For the 2,6-diacetylpyridinedihydrazone complexes of Sm, Eu and Gd nitrates, the separation in this region is  $25\text{ cm}^{-1}$ , which is a typical value for monodentate nitrates. The appearance of two strong bands at *ca.*  $1455$  and  $1310\text{ cm}^{-1}$  along with absorption at  $818\text{ cm}^{-1}$  confirms the binding of the nitrate groups in the monodentate fashion.

The spectrum of the ligand in the region between  $390$  and  $250\text{ cm}^{-1}$  contains only two weak bands at  $285$  and  $330\text{ cm}^{-1}$ . This would indicate that the additional band observed in the region  $390$ – $350\text{ cm}^{-1}$  in the spectra of all the lanthanide complexes should be assigned to the metal–nitrogen stretching vibration.

The broad diffuse band of medium intensity in the  $3600$ – $3500\text{ cm}^{-1}$  region is observed for all 1:2 complexes and is assigned to the symmetric and anti-

symmetric O–H stretching modes for lattice water. The spectra of all chloride and perchlorate complexes and the nitrate complexes of Sm, Eu and Gd exhibit a weak intensity band at  $900$ – $850\text{ cm}^{-1}$ , attributable to the coordinated water molecules. The presence of water bound in two different ways is supported by the results of thermogravimetric analysis. In the case of the 1:1 chloride and perchlorate complexes of La, the loss of six molecules of water is observed at  $150$ – $180^\circ\text{C}$ , whereas the 1:2 nitrate complexes of La, Ce, Pr and Nd indicate the loss of six molecules of lattice water below  $100^\circ\text{C}$ . All the 1:2 chloride and perchlorate complexes lose three water molecules at  $150$ – $180^\circ\text{C}$  and one molecule at  $70$ – $90^\circ\text{C}$ . The 1:2 complexes of Sm, Eu and Gd nitrates indicate the loss of one mole of water per mole of metal ion in the temperature range of  $150$ – $170^\circ\text{C}$  and the loss of two water molecules below  $100^\circ\text{C}$ .

The electronic spectra of all the complexes recorded in acetonitrile (Table II and III) show similar features, containing an intense and medium absorption bands with maxima at  $275$ – $287\text{ nm}$  and  $347$ – $360\text{ nm}$ , respectively. The free ligand shows an intense band at  $273\text{ nm}$  with a shoulder at  $305\text{ nm}$  attributable to intraligand  $\pi \rightarrow \pi^*$  transition located mainly on the  $\text{C}=\text{N}$  group [9, 11]. The shift of this absorption band in the complexes relative to the free ligand and the occurrence of a band at *ca.*  $350\text{ nm}$  responsible for the colour of the complexes can be explained by the metal–ligand interaction.

The  $^1\text{H}$  NMR spectrum of the diamagnetic  $[\text{LaL}_2(\text{NO}_3)_3] \cdot 2\text{H}_2\text{O}$  complex obtained in  $\text{DMSO-d}_6$  shows a small downfield shift of the methyl and pyridine protons to  $\delta$  2.35 and 8.2, respectively, compared to the corresponding signals in the free ligand (see Experimental). This fact further supports the coordination of azomethine and pyridine nitrogen atoms to the metal ion [8, 11].

## Conclusions

On the basis of available evidence it seems reasonable to conclude that in all the complexes of lanthanides the 2,6-diacetylpyridinedihydrazone acts as a terdentate NNN donor ligand. The stoichiometry of the complexes depends on the kind of central atom, the type of counterion and the preparative conditions. The tentative coordination number of nine is assigned for the 1:2 La, Ce, Pr, Nd, Sm, Eu and Gd complexes of hydrazone with non-coordinating chlorides and perchlorates as counterions, assuming the filling of the coordination sphere by two molecules of ligand and three water molecules. In the case of lanthanum, a 1:1 complex is also isolated with chloride and perchlorate as counterions. These complexes also contain nine-coordinate metal ion, if we assume all the water molecules to be coordinated.

With the small but strongly coordinating nitrate ions, the lighter lanthanides (La to Gd) form 2,6-

diacetylpyridinedihydrazone complexes with stoichiometry metal:ligand of 1:2, whereas the heavier lanthanides (Tb to Lu) [10] yield 1:1 complexes, irrespective of the molar ratios of the starting materials used in the synthesis. The tentative coordination number of twelve is achieved in La, Ce, Pr and Nd complexes by incorporation of three bidentate nitrate groups in the coordination sphere. In the 1:2 hydrazone complexes of Sm, Eu and Gd, the three nitrate groups coordinate in the monodentate fashion and the tentative coordination number of ten is assigned, assuming the coordination of one molecule of water.

Thus the final geometry of lanthanide complexes depends on a variety of effects. Of these, the complexing properties of counterions seem to play an important role in the stabilization of a particular symmetry around the lanthanide ion.

#### Acknowledgement

This research was supported by the Polish Academy of Sciences (Project C.P.B.P. No. 01.12.4.18.).

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