

Synthesis, spectroscopic studies, and crystal structure of 2,6-diacetylpyridinediphenylhydrazone perchlorate and its complexing ability toward the lanthanides

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Abstract 2,6-diacetylpyridinediphenylhydrazone perchlorate was prepared and characterized by spectroscopic (IR, ESI-MS, UV-Vis, ^1H NMR) and analytical data and its crystal structure was determined by single X-ray analysis. The lanthanum(III), praseodymium(III), and neodymium(III) perchlorate complexes of 2,6-diacetylpyridinediphenylhydrazone were prepared in a direct reaction of the ligand with appropriate metal perchlorates. The spectroscopic and analytical data indicate 1:2 metal to ligand stoichiometry. In all the complexes the hydrazones act as monodeprotonated terdentate NNN donor chelators. The same lanthanum(III) complex was also obtained in a one-step condensation reaction between 2,6-diacetylpyridine and phenylhydrazine in the presence of lanthanum(III) perchlorate.

Keywords La(III) · Pr(III) · Nd(III) · Hydrazones · Spectroscopy · Crystal structure

Introduction

The chemistry of hydrazones has been intensively investigated in recent years, owing to their chelating capability and pharmacological activity. Hydrazones are used in analytical chemistry as highly selective extractants, luminescent probes, and molecular sensors [1–5]. They have proved to possess antibacterial, antifungal, and antitumor properties

[6–10] and have been suggested as possible therapeutics for the treatment of genetic and neurodegenerative disorders such as thalassemia and Alzheimer disease [11–14]. Continuing our investigation of the macrocyclic and acyclic lanthanide Schiff base complexes in view of their potential application in chemical, biochemical, and medical sciences and technology [15, 16] we describe here the synthesis, spectral characterization, and X-ray crystal structure of the 2,6-diacetylpyridinediphenylhydrazone perchlorate and its chelating behavior toward the lanthanum(III), praseodymium(III), and neodymium(III) ions.

Experimental

Materials

2,6-diacetylpyridine (Aldrich Chemical Company) and phenylhydrazine (Fluka) were used as received. The hydrated lanthanum(III), praseodymium(III), and neodymium(III) perchlorates were prepared by dissolving the 99.99% oxides (Fluka) in a slight excess of perchloric acid (Fluka). The solutions were evaporated and the precipitates were recrystallized from methanol.

Physical measurements

IR spectra were recorded using KBr pellets in the range of 4000–400 cm^{-1} on a Bruker IFS 66v/S spectrophotometer. Electrospray mass spectra were determined in methanol using a Waters Micromass ZQ spectrometer. The concentrations of the compounds were about 10^{-4} mol dm^{-3} . Sample solutions were introduced into the mass spectrometer source with a syringe pump with a flow rate of 40 $\mu\text{L min}^{-1}$ with a capillary voltage of +3 kV and

Dedicated to Professor Adam Bartecki on the occasion of his 90th birthday.

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desolvation temperature of 300 °C. The source temperature was 120 °C. Cone voltage (V_c) was set to 30 V to allow transmission of ions without fragmentation processes. Scanning was performed from $m/z = 200$ –1000 over 6 s, and 10 scans were summed to obtain the final spectrum. ^1H NMR spectra were recorded in CD_3CN on a Varian Gemini 300 spectrometer with chemical shift (ppm) reported relative to TMS as an internal reference. Electronic absorption spectra were measured on a JASCO V-550 spectrophotometer in methanol. Microanalyses (CHN) were obtained using a Perkin-Elmer 2400 CHN microanalyzer.

X-ray structure analysis

Diffraction data were collected at 100(1) K by the ω -scan technique, on a KUMA-KM4CCD diffractometer [17] with graphite-monochromatized MoK_α radiation ($\lambda = 0.71073$ Å). The temperature was controlled by an Oxford Instruments Cryosystems cooling device. The data were corrected for Lorentz-polarization effects as well as for absorption [17]. Accurate unit-cell parameters were determined by a least-squares fit of 6866 reflections of highest intensity, chosen from the whole experiment. The structure of 2,6-diacetylpyridinediphenylhydrazone perchlorate was solved with SIR92 [18] and refined with the full-matrix least-squares procedure on F^2 by SHELXL97 [19]. Scattering factors incorporated in SHELXL97 were used. The function $\sum w(|F_o|^2 - |F_c|^2)^2$ was minimized, with $w^{-1} = [\sigma^2(F_o)^2 + 0.045 \cdot P^2]$, where $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were located in subsequent difference Fourier maps and their positional and isotropic displacement parameters were freely refined. Relevant crystal data are listed in Table 1, together with refinement details.

Preparation of the 2,6-diacetylpyridinediphenylhydrazone perchlorate $\text{H}_3\text{LClO}_4 \cdot 0.5\text{H}_2\text{O}$

To a solution of 2,6-diacetylpyridine (32.6 mg, 0.2 mmol) in methanol (5 mL) phenylhydrazine (0.0724 mL, 0.4 mmol) was added dropwise with stirring. The reaction was refluxed for about 2 h. The yellow precipitate was filtered, washed with diethyl ether, and dried on air. This was dissolved in methanol and to this solution HClO_4 (0.02 mL) was added. After 2 days red crystals suitable for X-ray diffraction analysis were isolated and dried on air. Yield: 85%. Anal. Calc. (%) for $\text{H}_3\text{LClO}_4 \cdot 0.5\text{H}_2\text{O}$: C, 55.69; H, 5.12; N, 15.46. Found (%): C, 55.56; H, 5.10; N, 15.40; m/z (ESI): 344 ($\text{H}_2\text{L} + \text{H}$) $^+$; ν_{max} (KBr)/ cm^{-1} : 3540 (OH), 3104, 3057, 3011 (N–H), 1590 (C=N), 1545, 1457, 977, 636 (py), 1164 (N–N), 1114, 624 (ClO_4^-); δ_{H} (300 MHz; CD_3CN): 9.06 (2H, NH), 8.08–7.7 (3H, py),

Table 1 Crystal data, data collection, and structure refinement for $2\text{H}_3\text{L}^+ \cdot 2\text{ClO}_4^- \cdot \text{H}_2\text{O}$

| | |
|--|--|
| Compound | $2\text{H}_3\text{L}^+ \cdot 2\text{ClO}_4^- \cdot \text{H}_2\text{O}$ $\text{H}_3\text{L} \cdot \text{ClO}_4 \cdot 0.5\text{H}_2\text{O}$ |
| Formula | $2(\text{C}_{21}\text{H}_{22}\text{N}_5^+) \cdot 2(\text{ClO}_4^-) \cdot \text{H}_2\text{O}$ |
| Formula weight | 905.79 |
| Crystal system | Triclinic |
| Space group | P-1 |
| a (Å) | 7.2311(5) |
| b (Å) | 13.6736(10) |
| c (Å) | 21.6067(15) |
| α (°) | 91.585(6) |
| β (°) | 95.345(6) |
| γ (°) | 100.049(6) |
| V (Å 3) | 2092.3(3) |
| Z | 2 |
| D_x (g cm^{-3}) | 1.44 |
| $F(000)$ | 948 |
| μ (mm^{-1}) | 0.225 |
| Crystal size (mm) | 0.3 × 0.2 × 0.15 |
| Θ range (°) | 2.84–29.27 |
| hkl range | $-9 \leq h \leq 7$ $-18 \leq k \leq 17$ $-29 \leq l \leq 28$ |
| Reflections | |
| Collected | 15761 |
| Unique (R_{int}) | 9849 (0.017) |
| With $I > 2\sigma(I)$ | 6643 |
| No. of parameters | 749 |
| $R(F)$ [$I > 2\sigma(I)$] | 0.038 |
| $wR(F^2)$ [$I > 2\sigma(I)$] | 0.084 |
| $R(F)$ [all data] | 0.065 |
| $wR(F^2)$ [all data] | 0.089 |
| Goodness of fit | 0.955 |
| max/min $\Delta\rho$ ($\text{e} \text{ \AA}^{-3}$) | 0.40/–0.45 |

7.29–6.88 (10H, phen), 2.49 (6H, CH_3); λ_{max} (MeOH)/nm ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$): 216.5 (19120), 344.5 (43480).

Direct synthesis of La(III), Pr(III), and Nd(III) perchlorate complexes of H_2L

All the complexes were synthesized following the same general procedure. $\text{H}_3\text{L} \cdot \text{ClO}_4 \cdot 0.5\text{H}_2\text{O}$ (9 mg, 0.02 mmol) in methanol (5 mL) was added dropwise with stirring to a solution of La(III), Pr(III) or Nd(III) perchlorate hexahydrate (54.5 mg, 54.73 mg or 55.06 mg, 0.02 mmol) in methanol (5 mL). The reactions were carried out for 24–48 h and red precipitates formed. These were filtered off, washed with diethyl ether, and dried on air. Yields: 65–75%. Anal. Calc. (%) for $\text{La}(\text{HL})_2(\text{ClO}_4)_4 \cdot 4\text{H}_2\text{O}$: C, 50.69; H, 4.86; N, 14.07. Found (%): C, 51.35; H, 4.93; N, 13.92; m/z (ESI): 344

($\text{H}_2\text{L} + \text{H}$)⁺, 171 ($\text{LaH}_2\text{L}\cdot\text{CH}_3\text{OH}$)³⁺; $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$: 3440, 866 (OH), 3108, 3060, 3010 (N–H), 1543 (C=N), 1573, 1459, 998, 647 (py), 1175 (N–N), 1088, 627 (ClO_4^-), 453 (La–N); $\delta_{\text{H}}(300 \text{ MHz}; \text{CD}_3\text{CN})$: 9.22 (2H, NH), 8.43–7.81 (6H, py), 7.26–6.85 (20H, phen), 2.49 (12H, CH_3); $\lambda_{\text{max}}(\text{MeOH})/\text{nm}$ ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$): 238.5 (36545), 349 (85827). Anal. Calc. (%) for $\text{Pr}(\text{HL})_2(\text{ClO}_4)\cdot 5\text{H}_2\text{O}$: C, 49.69; H, 4.96; N, 13.80. Found (%): C, 49.99; H, 4.94; N, 13.60; m/z (ESI): 344 ($\text{H}_2\text{L} + \text{H}$)⁺, 185 ($\text{PrH}_2\text{L}\cdot 4\text{H}_2\text{O}$)³⁺; $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$: 3400, 870 (OH), 3105, 3057, 3008 (N–H), 1541 (C=N), 1571, 1462, 999, 648 (py), 1176 (N–N), 1091, 624 (ClO_4^-), 430 (Pr–N); $\lambda_{\text{max}}(\text{MeOH})/\text{nm}$ ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$): 220 (22490), 348.5 (47338). Anal. Calc. (%) for $\text{Nd}(\text{HL})_2(\text{ClO}_4)\cdot 3\text{H}_2\text{O}$: C, 51.34; H, 4.72; N, 14.26. Found (%): C, 51.77; H, 4.77; N, 14.08; m/z (ESI): 344 ($\text{H}_2\text{L} + \text{H}$)⁺, 173 ($\text{NdH}_2\text{L}\cdot 4\text{CH}_3\text{OH}$)³⁺, 283 ($\text{NdH}_2\text{L}\cdot \text{H}_2\text{O}$)³⁺; $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$: 3439, 870 (OH), 3110, 3050, 3012 (N–H), 1542 (C=N), 1575, 1472, 997, 647 (py), 1174 (N–N), 1101, 627 (ClO_4^-), 435 (Nd–N); $\lambda_{\text{max}}(\text{MeOH})/\text{nm}$ ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$): 220 (22752), 348.5 (53091).

In situ synthesis of La(III) perchlorate complex of H_2L

To a mixture of 2,6-diacetylpyridine (16.3 mg, 0.1 mmol) in methanol (5 mL) and phenylhydrazine (0.0362 mL, 0.2 mmol) in methanol (5 mL), lanthanum(III) perchlorate hexahydrate (54.5 mg, 0.1 mmol) was added dropwise with stirring. The reaction was carried out for 24 h. The resulting red precipitate was filtered off, washed with ether, and dried on air. Yield: 55%. Anal. Calc. (%) for $\text{La}(\text{HL})_2(\text{ClO}_4)_3\cdot 3\text{H}_2\text{O}$: C, 51.62; H, 4.74; N, 14.33. Found (%): C, 52.47; H, 4.64; N, 14.43; m/z (ESI): 344 ($\text{H}_2\text{L} + \text{H}$)⁺, 171 ($\text{LaH}_2\text{L}\cdot\text{CH}_3\text{OH}$)³⁺; $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$: 3440, 866 (OH), 3105, 3060, 3010 (N–H), 1540 (C=N), 1580, 1460, 998, 647 (py), 1175 (N–N), 1090, 622 (ClO_4^-), 451 (La–N); $\delta_{\text{H}}(300 \text{ MHz}; \text{CD}_3\text{CN})$: 9.16 (2H, NH), 8.43–7.80 (6H, 9.29–6.88 (20H, phen), 2.49 (12H, CH_3); $\lambda_{\text{max}}(\text{MeOH})/\text{nm}$ ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$): 238.5 (14316), 349 (34520).

Results and discussion

2,6-diacetylpyridinediphenylhydrazone with the set of potential NNN donor atoms was obtained as its perchlorate salt by the Schiff base condensation of 2,6-diacetylpyridine with phenylhydrazine and identified by spectral data and X-ray crystal structure determination. The formulation of this compound as $\text{H}_3\text{L}\cdot\text{ClO}_4\cdot 0.5\text{H}_2\text{O}$ is in agreement with elemental analysis data.

In the crystal structure there are two cations and two anions in the asymmetric part of the unit cell and one water molecule; thus this compound may be formulated as $2\text{H}_3\text{L}^+\cdot 2\text{ClO}_4^-\cdot \text{H}_2\text{O}$ (Table 1).

Figure 1 shows the anisotropic ellipsoid representations of one of the symmetry-independent H_3L^+ cations. Some relevant geometric parameters are listed in Table 2.

The geometry of the two H_3L^+ cations is very similar and the position of protonation is in both cases confirmed by the successful refinement of hydrogen atom as well as by the geometrical features of its neighborhood. The significant differences between the symmetry-independent molecules are found only at the level of their conformations. These can be described by the dihedral angles between the planar fragments: three rings I, II, and III and two planar bridging fragments C(ar)–C=N–N–C(ar) (cf. Fig. 1, Table 2). All these fragments are almost perfectly planar, with the maximum deviation from the least-squares plane of 0.0105(11) Å, with the noticeable exception of fragment C6B–C61B=N61B–N62B–C63B which is significantly folded (deviations from the mean plane as large as 0.0735(10) Å). Molecule B is significantly more folded than A (Fig. 2); Table 2 lists some of the relevant torsion angles. It might be noted that while one part of the molecule is similar, the other part is fairly different.

In the crystal structure, the electrostatic interactions between charged species and relatively weak hydrogen bonds (Table 3) are the main factors determining the packing.

Independent molecules make separate and different motifs. Cation A with anion A and water molecule create a hydrogen-bonded “ladder” which extends along the [100] direction (Fig. 3a). In contrast, cation B with anions B make hydrogen-bonded centrosymmetric dimers which do not expand further (Fig. 3b).

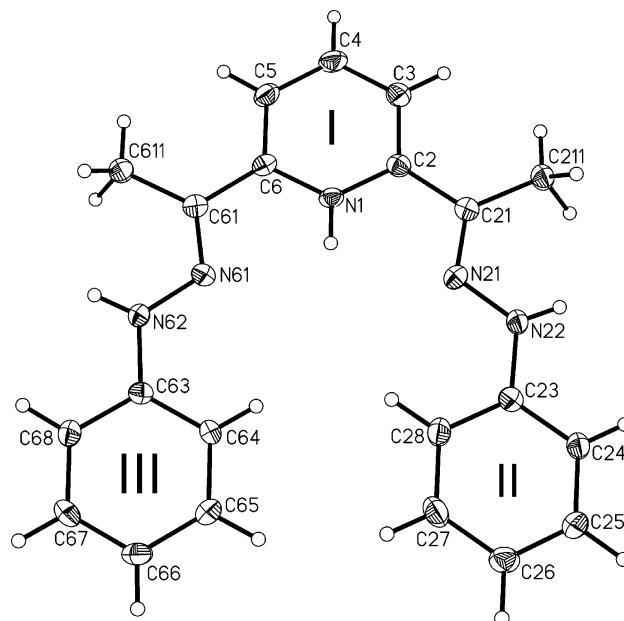
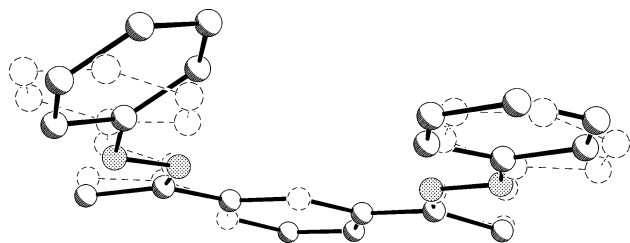


Fig. 1 Perspective view of one of the H_3L^+ cations (A) together with the labelling scheme [20]. Ellipsoids are drawn at the 50% probability level; hydrogen atoms are shown as spheres of arbitrary radii

Table 2 Selected geometrical parameters (Å, °) with e.s.d.'s in parentheses for $2\text{H}_3\text{L}^+\cdot 2\text{ClO}_4^-\cdot \text{H}_2\text{O}$

| | Molecule A | Molecule B |
|-----------------------|-------------|-------------|
| N1–C2 | 1.356(2) | 1.356(2) |
| N1–C6 | 1.361(2) | 1.347(2) |
| C21–N21 | 1.301(2) | 1.295(2) |
| N21–N22 | 1.336(2) | 1.343(2) |
| N22–C23 | 1.397(2) | 1.397(2) |
| C61–N61 | 1.300(2) | 1.299(2) |
| N61–N62 | 1.341(2) | 1.341(2) |
| N62–C63 | 1.397(2) | 1.397(2) |
| C2–N1–C6 | 125.03(14) | 125.69(15) |
| C21–N21–N22 | 117.70(14) | 119.20(14) |
| N21–N22–C23 | 121.52(15) | 120.56(14) |
| C2–C21–N21–N22 | 179.15(14) | –179.97(13) |
| C21–N21–N22–C23 | –179.40(14) | –179.58(14) |
| C6–C61–N61–N62 | 179.44(13) | –174.66(13) |
| C61–N61–N62–C63 | –179.86(15) | –168.82(14) |
| I/II | 7.05(5) | 2.52(7) |
| I/III | 3.14(9) | 12.74(12) |
| II/III | 4.36(5) | 31.26(7) |
| III/C(ar)–C=N–N–C(ar) | 0.08(8) | 21.30(16) |

**Fig. 2** Comparison of two symmetry-independent H_3L^+ cations [20]. The central pyridine rings were overlapped one onto another. *Solid lines*—molecule B, *dashed*—molecule A**Table 3** Hydrogen bond data (Å, °) for $2\text{H}_3\text{L}^+\cdot 2\text{ClO}_4^-\cdot \text{H}_2\text{O}$

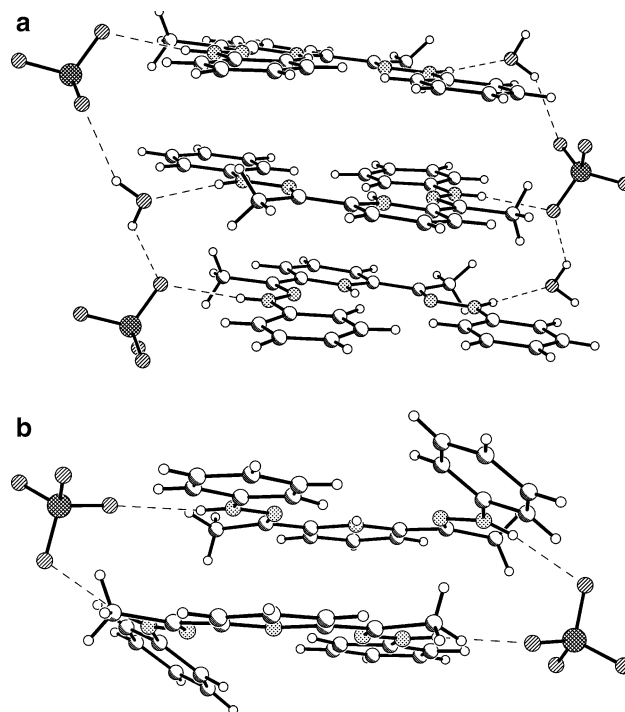
| D | H | A | D–H | D...A | H...A | D–H...A |
|--|------|-------------------|-----------|----------|-----------|-----------|
| $2\text{H}_3\text{L}^+\cdot 2\text{ClO}_4^-\cdot \text{H}_2\text{O}$ | | | | | | |
| N22A | H22A | O13 ^a | 0.800(18) | 3.119(2) | 2.345(18) | 162.9(17) |
| N62A | H62A | O1 W ^b | 0.853(18) | 3.075(2) | 2.246(19) | 163.9(16) |
| N22B | H22B | O23 ^b | 0.868(19) | 3.226(2) | 2.37(2) | 168.8(17) |
| N62B | H62B | O24 ^c | 0.874(17) | 3.059(2) | 2.224(18) | 159.9(15) |
| O1W | H1W1 | O13 | 0.95(4) | 3.111(2) | 2.31(4) | 142(3) |
| O1W | H1W2 | O12 ^d | 0.90(4) | 3.065(2) | 2.26(4) | 149(3) |

Symmetry codes: ^a $x, y-1 + z$; ^b $1-x, 1-y, 1-z$; ^c $-1 + x, 1 + y, z$; ^d $1 + x, y, z$

In both ladders and dimers relatively short π – π interactions provide additional stabilization. The distances between the planes of parallel (or almost parallel) rings are

as short as 3.39 Å for A...A and 3.32 Å and 3.35 Å for B...B. Also here the patterns are different. For the ladders ($\sim A \sim A \sim A \sim$) the terminal rings II and III overlap one over another, while for dimers the interactions take place between the central ring I and the terminal ring II which are almost coplanar with the central ring. In the latter case there is also π – π interaction, of similar kind (i.e., connecting the central and terminal rings) between the neighboring dimers. Comparison of these motifs can rationalize the differences in the conformations: the more folded cation B does not require the water molecule to catch the anions by means of hydrogen bonds.

In order to investigate the chelating behavior toward lanthanide metal centers, 2,6-diacetylpyridinediphenylhydrazone was allowed to react with lanthanum(III), praseodymium(III) or neodymium(III) perchlorate in methanol. The complexes were isolated as powder solids and characterized by spectroscopic and elemental analysis data. The complexes appear to have 1:2 lanthanide ion to ligand stoichiometry. Elemental analysis figures are consistent with the $\text{La}(\text{HL})_2(\text{ClO}_4)\cdot 4\text{H}_2\text{O}$, $\text{Pr}(\text{HL})_2(\text{ClO}_4)\cdot 5\text{H}_2\text{O}$, and $\text{Nd}(\text{HL})_2(\text{ClO}_4)\cdot 3\text{H}_2\text{O}$ formulae. The presence of one perchlorate counterion in all the complexes which balances the charge of the metal cation indicates that ligands exist in a monodeprotonated (HL^-) form. The ESI mass spectra provide strong evidence for the formation of the complexes. All the spectra exhibit peaks corresponding to the multiply charged species

**Fig. 3** Supramolecular motifs created by different molecules: **a** molecule A, **b** molecule B. Hydrogen bonds are shown as *dashed lines*

containing the metal ions coordinated to the ligand and the peaks assignable to the free ligand. To elucidate the coordination mode of 2,6-diacetylpyridinediphenylhydrazone spectral characterization of the complexes was performed with reference to the free ligand. The IR spectra of the complexes taken in the 4000–400 cm^{-1} region are all very similar to one another indicating the same bonding fashion of the ligand in all the complexes. The most significant variation between the free ligand and complexes concerns the $\nu(\text{C}=\text{N})$, $\nu(\text{N}-\text{N})$, and pyridine ring vibrations. The band at 1590 cm^{-1} in the free ligand attributable to $\nu(\text{C}=\text{N})$ stretching vibration is shifted by 47–50 cm^{-1} to lower frequencies upon complexation as expected for reduction of the electron density on the nitrogen atom due to coordination with the metal cations. The N–N stretching frequency found at 1164 cm^{-1} in the ligand increases by 10–12 cm^{-1} in the complexes suggesting the involvement of one of the nitrogen atoms of each N–N bond in the coordination. This causes reduction in electron repulsion by the lone pairs on adjacent nitrogen atoms. Evidence for the coordination of the pyridine nitrogen in the complexes comes from the increase in the frequency of high and low energy pyridine ring vibrations in the complexes compared to the free ligand. The spectra of all the complexes exhibit medium to strong bands at 1580–1459 cm^{-1} as expected for the high energy ring vibration of the coordinated pyridine. The bonding of the pyridine nitrogen atom is also shown by the presence of the band at 999–997 cm^{-1} and 648–647 cm^{-1} , attributable to the ring breathing frequency and the low energy pyridine ring vibration, respectively. The participation of the nitrogen atom in the metal–ligand coordination is further supported by the occurrence of bands at 453–430 cm^{-1} associated with metal–nitrogen vibration which are not seen in the spectrum of the free ligand. All the complexes show a broad diffuse band centered at 3440–3400 cm^{-1} due to the stretching and bending modes of the lattice and/or coordinated water. In addition, weak bands occur at the 870–866 cm^{-1} region which may be assigned to rocking or wagging modes of water molecules interacting with the metal ion. The presence of uncoordinated perchlorates is inferred from a very strong band at 1101–1088 cm^{-1} and a sharp medium band at 627–622 cm^{-1} . No splitting of the Cl–O stretching mode is observed as would be expected for coordinated perchlorate groups.

The coordination mode deduced by means of IR spectral data is confirmed by the deshielding of the pyridine and NH protons in the ^1H NMR spectrum of the diamagnetic lanthanum complex as compared with that of 2,6-diacetylpyridinediphenylhydrazone. The effect of coordination influences the chemical shifts in the complex, particularly for the signals which are related to the protons close to the donor sites. The downfield shift of these proton resonances is assumed to be a consequence of the coordination of the

ligands to the metal ion through the nitrogen atoms. The integrated intensities of the proton signals are in good agreement with the required ratios.

The electronic spectra of the free ligand and its complexes in methanol contain absorption bands assigned to the $\pi \rightarrow \pi^*$ transition of the pyridine ring and the imine groups. The higher and lower energy bands observed at 216.5 and 344.5 nm in the ligand display small bathochromic (red) shift as a result of changes in energy levels of ligand orbitals upon coordination of nitrogen atoms.

On the basis of the available data it seems reasonable to assume the analogous terdentate NNN donor behavior of 2,6-diacetylpyridinediphenylhydrazone in all the lanthanide complexes. The high coordination number typical of lanthanide ions, which has also been found in the relatively rare examples of structurally characterized complexes of these metal ions with related hydrazone ligands [21–24], is achieved by filling the coordination sphere by two terdentate monodeprotonated 2,6-diacetylpyridinediphenylhydrazone ligands with sufficient interaction of water molecules. Interestingly, we were also able to obtain the same lanthanum(III) complex containing two monodeprotonated 2,6-diacetylpyridinediphenylhydrazone ligand species as a result of a one-step Schiff base condensation reaction between 2,6-diacetylpyridine and phenylhydrazine carried out in the presence of lanthanum(III) perchlorate. It is worthy to note that we have found the lanthanide ions to be very efficient metal templates for the synthesis of Schiff base macrocyclic and acyclic complexes derived from suitable dicarbonyl compounds and amines [15]. This finding along with our earlier investigation confirms the usefulness of 2,6-diacetylpyridine as an excellent precursor for the formation of compounds with unusual properties and structures.

Supplementary material

CCDC-738988 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033; e-mail: deposit@ccdc.cam.ac.uk].

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