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Synthesis, crystal structures and magnetic behavior of Ni^{II}-4f-Ni^{II} compounds

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ABSTRACT

We report here synthesis, crystal and molecular structures as well as magnetic measurement results for new heterotrinuclear Schiff base complexes having a general formula $[Ni_2Ln(L)_2(CH_3COO)_2(MeOH)_2]$ -NO₃·4H₂O (where Ln = La^{III} (1) and Nd^{III} (2) and L = C₁₉H₁₈N₂O₄Br₂ = *N*,*N'*-bis(5-bromo-3-methoxysalicylidene)-1,3-diaminopropanato) and the mononuclear $[NiL(H_2O)_2]$ (3) complex. The Ni^{II}/4f compounds are isostructural and crystallize in the monoclinic space group *P*2₁/*n*. The lanthanide(III) ion lies on the center of symmetry and is ten-coordinated forming pentagonal antiprism. Compound 3 crystallizes in orthorhombic space group *Pnma* with the molecule lying on the mirror plane. The complex 1 indicated a weak antiferromagnetic interaction between the terminal Ni^{II} ions. The magnetic properties of 2 revealed that the Ni^{II}-Nd^{III} interaction is antiferromagnetic. The magnetic data for 3 show dominant zero-field splitting effect of Ni^{II} ions.

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1. Introduction

The studies on Ni^{II}-4f heteronuclear compounds are mainly focused on research their crystal structures and magnetic features [1–17]. The magnetic properties of heterotrinuclear Ni^{II}–Ln^{III}–Ni^{II} complexes (Ln^{III} from La^{III} to Lu^{III}) were studied by Shiga et al. and they indicated that the Ni^{II}-Ln^{III} interaction is weakly antiferromagnetic for $Ln^{III} = Ce^{III}$, Pr^{III} and Nd^{III} , and ferromagnetic for $Ln^{III} = Gd^{III}$, Tb^{III} , Dy^{III} , Ho^{III} and Er^{III} . Moreover, their magnetic studies of $Ni^{II}-Ln^{III}-Nj^{III}$ compounds with diamagnetic rare earth(III) ions (La^{III} and Lu^{III}) showed an antiferromagnetic interaction between the terminal Ni^{II} ions [1]. Pasatoiu et al. investigated a series of heterodinuclear Ni^{II}-Ln^{III} Schiff base complexes (Ln^{III} from La^{III} to Er^{III}) and stated that there are antiferromagnetic interactions between Ni^{II} and Ln^{III} ions for Ln^{III} from the beginning of the 4f series (Ce^{III}, Pr^{III}, Nd^{III}, Sm^{III}), while ferromagnetic occured from Gd^{III} toward the end of the 4f series [2]. Bayly, et al.'s magnetic studies of heterotrinuclear Ni^{II}-Ln^{III}-Ni^{II} compounds also showed the fer-romagnetic exchange between Ni^{II} and Gd^{III}, Tb^{III}, Dy^{III}, Ho^{III} or Er^{III} ions [5]. Kahn et al. observed with oxamato bridged Ni^{II}-Ln^{III} complexes that Ni^{II}-Ln^{III} interaction is antiferromagnetic for Ln^{III} = Ce^{III}, Pr^{III}, Nd^{III}, Er^{III} and ferromagnetic for Ln^{III} = Gd^{III}, Tb^{III}, Dy^{III} and perhaps Ho^{III} [8]. Chandrasekhar et al. reported the magnetic behavior of the Ni^{II}-Ln^{III}-Ni^{II} complexes (Ln^{III} from La^{III} to Er^{III}), the Ni^{II}-Ln^{III}-Ni^{II} (Ln^{III} = La^{III}, Ce^{III}, Pr^{III}, Nd^{III}, Sm^{III}, Eu^{III}, Ho^{III} and Er^{III}) were found to be simple paramagnetic systems, $Ni^{II}-Ln^{III}-Ni^{II}$ ($Ln^{III} = Gd^{III}$, Tb^{III}) compounds exhibit the ferromagnetic coupling, whereas the complex $Ni^{II}-Dy^{III}-Ni^{II}$ indicates a single-molecule magnet behavior [3].

In comparison to the magnetic studies of Cu^{II}–4f compounds [2,18,19] the magnetic properties of Ni^{II}–4f complexes have been much less investigated because many of these complexes contain a square planar Ni^{II} ion which is diamagnetic [7,20–23].

We have undertaken study on heteronuclear Ni^{II}–4f complexes in order to obtain more information on the crystal structures and magnetic properties of Ni^{II}–Ln^{III} Schiff base compounds. In the present paper we report the synthesis, structural characterization and magnetism of the heterotrinuclear [Ni₂La(L)₂(CH₃COO)₂ (MeOH)₂]NO₃·4H₂O (**1**) and [Ni₂Nd(L)₂(CH₃COO)₂(MeOH)₂]NO₃· 4H₂O (**2**) and the mononuclear [NiL(H₂O)₂] (**3**) complexes.

2. Experimental

2.1. Synthesis

2.1.1. Materials

The reagents and solvents *i.e.* 1,3-diaminopropane, 5-bromo-2hydroxy-3-methoxybenzaldehyde, Ni(CH₃COO)₂·4H₂O, La(NO₃)₃· 6H₂O, Nd(NO₃)₃·6H₂O and methanol used for synthesis were commercially available from Aldrich Chemical Company and Polish Chemical Reagents. They were used as received without further purification.





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2.1.2. N,N'-bis(5-bromo-3-methoxysalicylidene)propylene-1,3diamine, H₂L

The Schiff base (N,N'-bis(5-bromo-3-methoxysalicylidene) propylene-1,3-diamine, $C_{19}H_{20}Br_2N_2O_4$) abbreviated as H_2L was obtained by the 2:1 condensation of 5-bromo-2-hydroxy-3-methoxybenzaldehyde and 1,3-diaminopropane in methanol according to the reported procedure [18,19].

2.1.3. $[Ni_2La(L)_2(CH_3COO)_2(MeOH)_2]NO_3 \cdot 4H_2O(1)$

To a stirred solution of the Schiff base $H_2L(0.4 \text{ mmol}, 0.1999 \text{ g})$ in MeOH (30 mL) was added Ni(CH₃COO)₂·4H₂O (0.4 mmol, 0.0995 g) in MeOH (10 mL). As result the brown solid appeared. The obtained mixture was stirred for about 30 min, after this time the solution of La(NO₃)₃·6H₂O (0.2 mmol, 0.0866 g) in MeOH (5 mL) was added. The brown precipitate dissolved and solution turned pale-green. The resulting solution was left to stir for about 30 min. during which time it did not change color. The solution was then filtered and allowed to evaporate slowly at low temperature in the fridge (277 K). Pale-green crystals of 1 formed in three weeks. Yield: 97 mg/31%. Anal. Calc. (1568.84): C, 33.68; H, 3.70; N, 4.46; Ni, 7.48; La, 8.85. Found: C, 33.47; H, 3.46; N, 4.31; Ni, 7.57; La, 8.35%. FTIR bands (KBr, cm⁻¹): 3424m, 2932w, 2848w, 1644s, 1572w, 1468s, 1440m, 1384s, 1292s, 1236s, 1216m, 1104w, 1012w, 966w, 852w, 780m, 760w, 692w, 628w, 576w, 540w, 460m.

2.1.4. [Ni₂Nd(L)₂(CH₃COO)₂(MeOH)₂]NO₃·4H₂O (**2**)

Complex **2** was synthesized according to the procedure followed for **1** (Nd(NO₃)₃·6H₂O, 0.2 mmol, 0.0877 g). Yield: 102 mg/ 32%. *Anal.* Calc. (1574.17): C, 33.57; H, 3.68; N, 4.55; Ni, 7.46; Nd, 9.16. Found: C, 33.12; H, 3.36; N, 4.97; Ni, 7.10; Nd, 8.98%. FTIR bands (KBr, cm⁻¹): 3424m, 2932w, 2848w 1640s, 1572w, 1468s, 1440m, 1384s, 1292s, 1236s, 1216m, 1104w, 1012w, 966w, 852w, 780m, 760w, 692w, 628w, 576w, 540w, 460m.

2.1.5. $[NiL(H_2O)_2]$ (3)

Complex **3** was obtained by the treatment of Ni(CH₃COO)₂·4H₂O (0.2 mmol, 0.0498 g) in MeOH (10 mL) with H₂L (0.2 mmol, 0.0995 g) in 10 mL of hot MeOH (about 318 K). The reaction mixtures were stirred for about 30 min, cooled and the resulting brown precipitates were filtered off. The obtained solution was allowed to evaporate slowly at low temperature in the fridge (277 K). Pale-green crystals **3** formed over several days. Yield: 88 mg/74%. *Anal.* Calc. (592.88): C, 38.59; H, 3.38; N, 4.74; Ni, 9.93. Found: C, 38.12; H, 3.23; N, 4.56; Ni, 9.49%. FTIR bands (KBr, cm⁻¹): 3464m, 2932w, 2844w 1624s, 1540w, 1468s, 1432m, 1384s, 1292s, 1240s, 1216m, 1112m, 1012w, 972w, 828m, 784m, 768m, 688m, 628w, 576w.

2.2. Methods

The contents of carbon, hydrogen and nitrogen in the analysed compounds were determined by elemental analysis using a CHN 2400 Perkin Elmer analyser.

The contents of nickel and lanthanides were established using ED XRF spectrophotometer (Canberra–Packard).

The FTIR spectra of complexes were recorded over the range of $4000-400 \text{ cm}^{-1}$ using M-80 spectrophotometer (Carl Zeiss Jena). Samples for FTIR spectra measurements were prepared as KBr discs.

The magnetization of the (1), (2) and (3) powdered samples was measured over the temperature range 1.8–300 K using a Quantum Design SQUID – based MPMSXL–5-type magnetometer. The superconducting magnet was generally operated at a field strength ranging from 0 to 5 T. Measurements sample of compounds were made at magnetic field 0.5 T. The SQUID magnetometer was calibrated with the palladium rod sample. Corrections are based on subtracting the sample – holder signal and contribution χ_D estimated from the Pascal's constants [24].

2.3. X-ray crystal structure determination

Crystal data for 1, 2 and 3 were collected on Oxford Diffraction Xcalibur CCD diffractometer with the graphite-monochromatized Mo K α radiation (λ = 0.71073 Å) at the temperatures of 100(2) K (1, 2) and 300(2) K (3). Data sets were collected using the ω scan technique, with an angular scan width of 1.0°. The programs CrysAlis CCD and CrysAlis Red [25] were used for data collection, cell refinement and data reduction. Analytical absorption correction based on the indexing of crystal faces was applied for 1-3 [26]. The structures were solved by direct methods using SHELXS-97 and refined by the full-matrix least-squares on F^2 using the SHELxL-97 [27] (both operating under WinGX [28]). Non-hydrogen atoms with except of disordered nitrate N and O atoms and one water molecule in 1 and 2 were refined with anisotropic displacement parameters. The Nd ion in 1 and 2 lies on the center of inversion with sof = 0.5. The nitrate ion is disordered over two positions by the center of inversion (sof's = 0.5). Because of disorder in nitrate molecule the bond length restraints were applied by DFIX instructions to 1.23(1) Å and 2.13(1) Å for N-O and O-O distances, respectively. In 3 the mirror plane bisects the molecule through Ni1, C9, O3 and O4 atoms (sof's = 0.5). The C-bound H atoms were included in calculated positions and treated as riding atoms: C-H = 0.93-0.99 Å, with $U_{iso}(H) = 1.2 U_{eq}(C)$ or =1.5 $U_{eq}(C)$ for methyl H atoms. The O-bound H atoms were located in a difference Fourier map and refined using a riding model with O-H distances of 0.82-0.85 Å and $U_{iso}(H) = 1.5 U_{eq}(O)$. A summary of data collection conditions and the crystal structure refinement parameters are given in Table 1. The molecular plots were drawn with ORTEP3 for Windows [29] and Diamond [30].

3. Results and discussion

3.1. Description of crystal and molecular structure of the trinuclear complexes ${\bf 1}$ and ${\bf 2}$

The trinuclear Schiff base complexes $[Ni_2Ln(L)_2(CH_3COO)_2 (MeOH)_2]NO_3·4H_2O$ (where Ln = La^{III} (1) and Nd^{III} (2) and L = C₁₉H₁₈N₂O₄Br₂ = *N*,*N'*-bis(5-bromo-3-methoxysalicylidene)-1,3-diaminopropanato) are isostructural and crystallize in the monoclinic space group *P*2₁/*n*. Their schematic diagram is given in Fig. 1. The atom numbering scheme of **1** is shown in Fig. 2 (analogues for compound **2**). Details of the single crystal X-ray diffraction data collection and refinement are summarized in Table 1. The selected bond lengths and angles are given in Table 2. These trinuclear compounds consist of a cationic $[Ni_2Nd(L)_2(CH_3COO)_2(MeOH)_2]^+$ unit, one uncoordinated nitrate ion and four water molecules.

The lanthanide(III) ion lies on the center of inversion and is tencoordinated forming pentagonal antiprism (Fig. 3). It is surrounded by two Schiff base ligands. Comparing to our previously reported trinuclear complexes of $Cu^{II}-Ln^{III}-Cu^{II}$ (where $Ln^{III} = Ce^{III}$, Pr^{III} and Nd^{III}) with pentacoordinated Cu^{II} ions [19], the Schiff base molecules in heteronuclear Ni^{II} compounds are more flat and their relative position may be described as partly overlapped instead of propeller-like structure (Fig. 4). The organic ligand molecule is less distorted in Ni^{II}-4f-Ni^{II} complexes, thus the disorder of bridge carbon atoms is no longer observed. The dihedral angles between two phenyl rings in the Schiff base molecule are as follows (in °): 40 in 1 (Ni^{II}-La^{III}-Ni^{II}) and 38 in 2 (Ni^{II}-Nd^{III}-Ni^{II}) whereas in Cu^{II}-4f-Cu^{II} compounds they are 51 (Cu^{II}-Ce^{III}-Cu^{II}), 49 (Cu^{II}-Pr^{III}-Cu^{II}) and 52 (Cu^{II}-Nd^{III}-Cu^{II}), respectively.

Table 1						
Crystallographic	data	for	crystals	1, 3	2 and	3.

	1	2	3
Empirical formula	C44H58Br4N5O21Ni2La	C44H58Br4N5O21Ni2Nd	C ₁₉ H ₂₂ Br ₂ N ₂ O ₆ Ni
Formula weight	1568.84	1574.17	592.88
T (K)	100(2)	100(2)	300(2)
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/n$	$P2_1/n$	Pnma
a (Å)	13.682(1)	13.706(1)	7.583(2)
b (Å)	15.461(1)	15.525(1)	24.312(5)
<i>c</i> (Å)	14.831(1)	14.761(1)	11.619(4)
β (°)	117.11(1)	117.34(1)	90
V (Å ³)	2792.6(4)	2790.1(4)	2142(1)
Ζ	2	2	4
Crystal form/colour	block/green	block/green	block/green
Crystal size (mm)	$0.35 \times 0.25 \times 0.20$	$0.38 \times 0.20 \times 0.18$	$0.10 \times 0.10 \times 0.08$
D_{calc} (g cm ⁻³)	1.866	1.874	1.838
μ (mm ⁻¹)	4.359	4.528	4.675
Absorption correction	analytical	analytical	analytical
θ range (°)	2.74-25.24	2.76-25.31	3.06-25.24
Reflections collected/ unique (R_{int})	22196/5046 (0.0387)	11001/5098 (0.0211)	7000/1983 (0.0991)
Data/restraints/parameters	5046 / 7 / 342	5068 / 7 / 342	1983 / 0 / 143
Goodness-of-fit (GOF) on F^2	1.067	1.056	1.031
$R_1 \ wR_2 \ [I > 2\sigma(I)]$	0.0521, 0.1462	0.0436, 0.1171	0.0830, 0.2079
R_1 w R_2 (all data)	0.0760, 0.1568	0.0582, 0.1221	0.1569, 0.2352
$\Delta ho_{\rm max}$, $\Delta ho_{\rm min}$ (e Å ⁻³)	1.633 (0.65 Å from H5B) and -1.330 (1.06 Å from Br1)	2.358 (1.01 Å from H5A) and -1.105 (0.96 Å from Br1)	2.044 (1.41 Å from O4) and -1.591 (0.92 Å from H3)

The rare earth(III) ion supplements its coordination environment by two acetate ions. Each pair of the Ni^{II} and Ln^{III} metal ions are linked by two bridging phenoxo oxygen atoms (O1 and O2) of the Schiff base ligand and one bidentate bridging carboxylate group (O6C2007) of the acetate ion.

Nickel(II) ion occupies the N₂O₂ compartment of the Schiff base. It has distorted octahedral geometry with methanol molecule and acetate anion (bridging to Ln^{III}) in apical positions. The Ni^{II} ion lies in the mean N1N2O1O2 plane of the Schiff base ligand with deviation being only 0.045 and 0.042 Å for **1** and **2**, respectively. While in Cu^{II}-Ce^{III}-Cu^{II}, Cu^{II}-Pr^{III}-Cu^{II} and Cu^{II}-Nd^{III}-Cu^{II} complexes the corresponding deviations for Cu^{II} ions are higher, *viz.* 0.148, 0.144 and 0.154 Å, respectively [19].

The M–O bond distances of Ni^{II} and La^{III}/Nd^{III} with bridging phenolate and carboxylate groups are significantly different (Ni–O *ca.* 2.0 Å, and La/Nd–O *ca.* 2.5 Å). Such differences in bond distance are



Fig. 1. Diagram of molecular structure of complexes **1** and **2** ($Ln = La^{III}$ for **1**, Nd^{III} for **2**).

expected due to their differences in ionic size and are observed in related 3d–4f compounds [2,3,7]. The Ln1–O bond lengths depend on the nature of the oxygen atoms and increase in sequence acetate < phenolato < methoxo (Table 2).

The dihedral angles (α) between the (O1Ni1O2) and (O1La1/Nd1O2) planes are *ca.* 23° and 26°, respectively (Table 2).

The intramolecular separations Ni1...Ln, and Ni1...Ni1^{*i*} (symmetry code (*i*) -x, -y, -z) being *ca*. 3.6/3.3 and 7.2/7.0 Å in **1** and **2**, respectively (Table 2) are within the normal ranges of values for polynuclear Ni^{II}-Ln^{III} complexes [2,3,7]. Intermolecular M...M



Fig. 2. Molecular structure and atom numbering scheme of complex **1**, displacement ellipsoids were drawn at 50% probability level, hydrogen spheres were drawn with an arbitrary radius. The nitrate ion and water molecules in the outer sphere were omitted for clarity. Molecule lies on the center of inversion thus only half of molecule is symmetry independent and was numbered in the picture.

Table 2

Selected geometric parameters (Å, $^\circ)$ in the coordination environments of metal centers.

Bond lengths	1	2	Bond lengths	3
Ln1-01	2.514(4)	2.450(4)	Ni1-01	2.006(7)
Ln1-02	2.521(4)	2.450(4)	Ni1-03	2.125(9)
Ln1-03	2.851(4)	2.857(4)	Ni1-04	2.13(1)
Ln1-04	2.902(4)	2.924(3)	Ni1-N1	2.063(9)
Ln1-07	2.477(6)	2.401(4)		
Ni1-N1	2.041(5)	2.037(4)		
Ni1-N2	2.032(5)	2.028(5)		
Ni1-01	2.036(4)	2.024(4)		
Ni1-02	2.047(4)	2.037(4)		
Ni1-06	2.067(5)	2.070(4)		
Ni1-08	2.158(5)	2.163(4)		
Ni1-Ln1	3.607(4)	3.254(4)		
Ni1Ni1 ⁱ	7.214(4)	7.049(4)		
Angles	1	2	Angles	3
Ni1-01-Ln1	104.4(2)	103.6(2)	01-Ni1-01 ⁱⁱ	85.9(4)
Ni1-02-Ln1	103.8(2)	103.2(1)	01-Ni1-N1	88.7(3)
01-Ln1-02	64.0(2)	64.9(1)	N1-Ni1-N1 ⁱⁱ	96.6(5)
N2-Ni1-N1	96.5(2)	96.4(2)	01-Ni1-03	91.2(3)
N2-Ni1-01	172.8(2)	172.5(2)	N1-Ni1-O3	88.5(3)
N2-Ni1-02	91.4(2)	91.9(2)	01-Ni1-04	91.3(3)
N1-Ni1-02	171.6(2)	171.2(2)	N1-Ni1-04	89.2(3)
01-Ni1-N1	90.4(2)	90.9(2)	03-Ni1-04	176.5(5)
01-Ni1-02	81.6(2)	80.8(1)		
01-Ni1-06	94.9(2)	93.8(2)		
02-Ni1-06	95.4(2)	95.9(2)		
N1-Ni1-06	87.8(2)	87.3(2)		
N2-Ni1-06	87.9(2)	88.6(2)		
N1-Ni1-08	90.1(2)	89.4(2)		
N2-Ni1-08	95.2(2)	96.1(2)		
01-Ni1-08	82.2(2)	82.0(2)		
02-Ni1-08	86.4(1)	86.7(1)		
06-Ni1-08	176.5(2)	174.6(2)		
01-Ln1-03	57.7(1)	57.7(1)		
02-Ln1-03	111.6(1)	112.0(1)		
07-Ln1-03	116.3(2)	117.2(1)		
01-Ln1-04	112.8(1)	113.6(1)		
02-Ln1-04	57.0(1)	57.1(1)		
03-Ln1-04	119.8(1)	119.3(1)		
07-Ln1-01	76.0(2)	78.0(1)		
07-Ln1-02	78.1(2)	80.4(1)		
07-Ln1-04	117.2(2)	118.2(1)		
α	23(2)	26(2)		

 α – dihedral angle between the O1Ni1O2 and O1Ln1O2 planes. Symmetry codes: ^{*i*}-*x*, -*y*, -*z*; ^{*ii*} *x*, -*y* + 1/2, *z*.

separations in the Ni^{II} - Ln^{III} - Ni^{II} structures indicate well separation of the trinuclear 3d-4f-3d cores (Table 2).

Because of special position of molecule in the unit cell two Ni^{II} and one Ln^{III} ions are arranged in a line, with a Ni1–Ln1–Ni1^{*i*} (symmetry code (*i*): -x, -y, -z) angle equal to 180° (Table 2). In the outer coordination sphere between nitrate ions and water molecules forms extensive network of hydrogen bonds (Table 3).

3.2. Description of crystal and molecular structure of the complex 3

The complex **3** [NiL(H₂O)₂] is built of one-nuclear units. A view of the complex **1** is shown in Fig. 5. Details of the single crystal X-ray diffraction data collection and refinement are summarized in Table 1 and the principal bond distances and angles are listed in Table 2. The mirror plane bisects molecule through C9, Ni1, O3 and O4 atoms. The Ni^{II} ion has octahedral coordination and occupies the N₂O₂ cavity of the Schiff base ligand. The larger compartment is occupied by water molecules which connect the mononuclear units by O–H...O hydrogen bonds into one-dimensional columns lying parallel to the *a* axis (Table 3, Fig. 6). Between aromatic rings there are π ... π stacking interactions with separation between best planes being equal to 3.57 Å.



Fig. 3. A view of coordination polyhedra in 1.



Fig. 4. A view showing partly overlapping two Schiff base units in complex 1.

Table 3Hydrogen bond parameters (Å, °) in 1, 2 and 3.

D–H…A	D-H	Н…А	D…A	<dha< th=""><th>Complex</th></dha<>	Complex
05-H5A012	0.85	2.10	2.858(7)	148.5(4)	1
05–H5B07 ⁱ	0.85	1.85	2.682(6)	166.4(3)	1
08-H805	0.85	1.91	2.682(6)	172.7(4)	1
012-H12B09 ⁱⁱ	0.85	1.94	2.708(7)	148.5(4)	1
05-H5A012	0.85	2.02	2.782(7)	149.2(4)	2
05–H5B07 ⁱ	0.85	1.99	2.819(6)	166.1(4)	2
08-H805	0.85	1.89	2.722(7)	165.2(4)	2
012–H12B…09 ⁱⁱ	0.85	1.98	2.826(7)	173.5(4)	2
03–H3…01 ⁱⁱⁱ	0.85	2.12	2.87(1)	145(1)	3
04–H4…02 ^{iv}	0.82	2.24	2.94(1)	143(1)	3

Symmetry codes: ^{*i*} -x, -y, -z; ^{*ii*}x + 1, y, z; ^{*iii*}x + 1/2, -y + 1/2, -z + 1/2, ^{*vi*}x - 1/2, y - 1/2, y - 1/2, -z + 1/2.

3.3. Magnetic properties

The magnetic susceptibility of Ni^{II}–La^{III}–Ni^{II} (1) has been measured in the temperature range of 1.8–300 K in a 0.5 T applied magnetic field. The data obtained for complex are represented in Fig. 7. The central ion in **1** is diamagnetic (La^{III}, f^0 , S = 0), therefore the magnetization in this sample results only from the two Ni^{II} (d^8 , S = 1) ions. The Ni^{II} ions are octahedrally coordinated and are expected to exhibit spin-only moments modified by the effects of second-order spin-orbit coupling, which leads to a *g* value in excess of 2 [31]. At the room temperature, the $\chi_m T$ product is equal to 2.32 cm³ mol⁻¹ K and it is consistent with only two S = 1 nickel(II) centers (the expected $\chi_m T$ value is 2.42 cm³ mol⁻¹ K with $g_{Ni} = 2.20$). The moment decreases only marginally from 300 to 25 K, below which a rather sharp drop to 0.767 cm³ mol⁻¹ K at 1.8 K due to the intramolecular interaction and/or the effect of zero-field splitting are observed. In this complex, the intramolecular



Fig. 5. Ortep view of molecule 3 showing octahedral coordination of Ni ion. Atoms Ni1, C9, O3 and O4 lie on the mirror plane and only half of the molecule is symmetrically independent.



Fig. 6. View along a direction. Stacking columns in 3.



Fig. 7. Temperature dependence of experimental $\chi_m T$ (\bigcirc) and χ_m^{-1} (\bullet) *vs T* for complex **1.** The solid line is the calculated curve derived from Eq. (1).

lar Ni...Ni distance is certainly large and may preclude any significant magnetic interactions between the nickel centers in the heterotrinuclear compound. The thermal dependence of $\chi_m T$ is characteristic of a small antiferromagnetic interaction since no maximum appears in the $\chi_m T$ vs T curve until 1.8 K. This apparent weak antiferromagnetic interaction may be mediated by the diamagnetic lanthanum(III) center. The examples in the literature [1,3–5,32] and previously reported by us heterotrinuclear complex, Cu^{II}–La^{III}–Cu^{II} [19] show, that the diamagnetic lanthanum(III) center are capable of mediating magnetic exchange between the metal(II) in heteronuclear compounds.

The magnetization curve for **1** measured at 2 K was reproduced with the Brillouin function for two centers of $S_{Ni} = 1$ (Fig. 8) and clearly confirm our previous assumption.

Magnetic analyses were carried out using the magnetic susceptibility expression (Eq. (1)) based on the isotropic Heisenberg model ($H = -2J\vec{S}_{Ni1} \cdot \vec{S}_{Ni2}$) [33]:

$$\chi_m = \frac{2Ng^2\beta^2}{kT} \left(\frac{5\exp(6J/kT) + \exp(2J/kT)}{5\exp(6J/kT) + 3\exp(2J/kT) + 1} \right) + N_\alpha \tag{1}$$



Fig. 8. Field dependence of the magnetization for complex **1**. The solid line is the Brillouin function for two independent S = 1 of Ni^{II}–La^{III}–Ni^{II} unit.

where β is the Bohr magneton, g is Lande factor, k is Boltzman's constant, I is exchange parameter and N_{α} is the temperature-independent paramagnetism of Ni^{II} ion. For simplicity, other small magnetic contributions (intermolecular interaction, single ion zero-field splitting, etc.) are included in parameter *I*. The best least-squares fit to the experimental data in whole temperature range (solid line in Fig. 7) is obtained with $J = -0.75 \text{ cm}^{-1}$, $g = 2.18 \text{ and } N_{\alpha} = 320 \times 10^{-6}$ as indicated by the solid curve in Figure. The agreement factor R is equal 5.29 × 10^{-4} ($R = \Sigma(\chi_{exp}T - \chi_{calc}T)^2 / \Sigma(\chi_{exp}T)^2$). The exchange value of complex **2** is in good agreement with the *I* value (-0.63 cm^{-1}) of the similar trinuclear complex $[Ni_2La(L)_2(NO_3)_3]$ (H₂O)₄]H₂O [1]. This result strongly suggests that weak antiferromagnetic intramolecular Ni Ni interactions in the trinuclear unit are present and are partially or totally responsible for the decrease of $\chi_m T$ product at low temperatures. Nevertheless, it is worth adding that the given values of *J* should be taken with caution as even the presence of a very weak anisotropy of Ni^{II} can enhance artificially its estimation.

The magnetic properties of the heterotrinuclear complex, Ni^{II}–Nd^{III}–Ni^{II} (**2**), was also determined over the temperature range of 1.8–300 K. Plots of magnetic susceptibility χ_m^{-1} and $\chi_m T$ product vs *T* are given in Fig. 9. The experimental $\chi_m T$ values at room temperature (3.71 cm³ mol⁻¹ K) approximately correspond to the calculated ones $\chi_m T = ((N\beta^2/3k)[2g_{Ni}^2S_{Ni}(S_{Ni}+1) + g_{Ln}^2J_{Ln}(J_{Ln}+1)])$ for uncoupled metal ions (3.64 cm³ mol⁻¹ K). The $\chi_m T$ decreases



Fig. 9. Temperature dependence of experimental $\chi_m T$ (\bigcirc) and χ_m^{-1} (\bullet) *vs T* for complex **2**.

by lowering the temperature to 0.933 cm³ mol⁻¹ K in 1.8 K. This decrease could be caused by crystal field effect, as well as cooperative antiferromagnetic interactions of Ni^{II}-Nd^{III} pairs. The susceptibility data obey the Curie-Weiss law with the Curie constant of C = $3.71 \text{ cm}^3 \text{ mol}^{-1}$ K and the Weiss constant of $\theta = -7.4$ K. Negative value of Weiss constant could also confirm the antiferromagnetic exchange coupling between the metal ions. Previously, we reported heterotrinuclear complex, Cu^{II}-Nd^{III}-Cu^{II} [19] and magnetic investigations also reveal a antiferromagnetic interaction between the Cu^{II} and Ln^{III} centres. These results are consistent with the empirical studies concerning heterometallic 3d-4f compounds, in which the 4f ions display a spin-orbit coupling [1,5,23,34-42]. A final conclusion on the nature of the exchange interaction in compounds cannot be drawn, since the magnetic properties of this type of systems are not only due to the coupling between the 3d and 4f metal ions, but also to the thermal depopulation of the Stark sublevels of the 4f ions.

To confirm the nature of the ground state of **2**, we investigated the variation of the magnetization, *M*, with respect to the field, at 2 K. The results are shown in Fig. 10, where molar magnetization M is expressed in $\mu_{\rm B}$ units. The compound does not reach the saturation in the applied field range and magnetization in 5 T is equal only to 3.52 $\mu_{\rm B}$. This value is much lower than the simulated values calculated with the Brillouin function for two Ni^{II} ions and one Nd^{III} ion, which do not interact. This further indicates that the complex behaves as an antiferromagnet. Unfortunately, the quantitative description of the magnetic properties of heterometallic complexes containing lanthanide(III) ions is not an easy task because of the ligand-field effect and spin-orbit coupling of the Ln^{III} ion [23,36].

The magnetic properties of the complex **3** was determined over the temperature range of 1.8–300 K. Plots of magnetic susceptibility χ_m^{-1} and $\chi_m T$ product vs *T* are given in Fig. 11. The value $\chi_m T$ of at 300 K equals 1.19 cm³ mol⁻¹ K and remains constant down to 20 K. The value of $\chi_m T$ in room temperature is larger than that expected for the spin-only formula for a mononuclear Ni^{II} complex (*S* = 1), indicating that a relevant orbital contribution is involved. The $\chi_m T$ product decreases significantly at lower temperatures, attaining a value of 0.362 cm³ mol⁻¹ K at 1.8 K. The decrease of the values $\chi_m T$ in the lowest temperature range is mainly due to zero-field splitting effect of Ni^{II} ions and probably weak antiferromagnetic intermolecular interactions between the Ni^{II} ions.

Since the decrease $\chi_m T$ in low temperature range can be attributed the zero-field splitting (ZFS) of Ni^{II} ions, we used the Hamiltonian (Eq. (2)) for an isolated Ni^{II} ion with S = 1:



Fig. 10. Field dependence of the magnetization for complex **2**. The solid line is the Brillouin function curve for a two independent S = 1 and one $S = {}^{3}/_{2}$ of Ni^{II}–Nd^{III}–Ni^{II} unit.



Fig. 11. Temperature dependence of experimental $\chi_m T(\bigcirc)$ and $\chi_m^{-1}(\bullet)$ vs *T* for complex **3.** The solid line is the calculated curve derived from Eqs. (3)–(6).



Fig. 12. Field dependence of the magnetization for complex **3**. The solid line is the Brillouin function curve for non coupled ions, the g-factor is taken 2.00 and S = 1.

$$H = D\left[\hat{S}_z^2 - \frac{1}{3}S(S+1)\right] + g\beta H\hat{S}$$
⁽²⁾

Developing the Hamiltonian (Eq. (2)) we can deduce the following expressions (Eqs. (3)–(5)) [43] for the magnetic susceptibility corrected by the factor predicted from the molecular field (Eq. (6)) [44]:

$$\chi_m = \frac{\chi_{\parallel} + 2\chi_{\perp}}{3} \tag{3}$$

$$\chi_{||} = \frac{2Ng_{||}^2\beta^2}{kT} \frac{\exp(-D/kT)}{1 + 2\exp(-D/kT)}$$
(4)

$$\chi_{\perp} = \frac{2Ng_{\perp}^{2}\beta^{2}}{D} \frac{1 - \exp(-D/kT)}{1 + 2\exp(-D/kT)}$$
(5)

$$\chi_m^{\rm corr} = \frac{\chi_m}{1 - \frac{2Zl'}{Nh^2 g^2} \cdot \chi_m} \tag{6}$$

where zJ' is the intermolecular exchange parameter and D (axial zero-field splitting parameter) is the energy difference between $M_s = \pm 1$ and $M_s = 0$ levels. The best fit leads to the values $|D| = 5.89 \text{ cm}^{-1}$ (the sign of D cannot be determined from powder magnetic susceptibility data), $zJ' = -0.77 \text{ cm}^{-1}$ and $g_{av} = 2.20$, indi-

cated as the solid curve in Fig. 11. The criterion used in determination of the best fit was based on minimization of the sum of squares of the deviation, $R = \Sigma(\chi_{exp}T - \chi_{calc}T)^2/\Sigma(\chi_{exp}T)^2$ ($R = 2.15 \times 10^{-4}$). A small, negative value of *zJ* obtained from calculations indicates occurrence of weak antiferromagnetic interactions between the nickel(II) ions in crystal lattice. Calculated zero-field splitting parameter of examined complex **3** equals 5.89 cm⁻¹ is typical for large group of monomeric complexes of the nickel(II), which indicates values of the parameter in the range 3–6 cm⁻¹ [45–48], however are known examples much lower values [49–51]. Nevertheless, the calculated *D* parameter is larger than *zJ* and suggests that in the compound studied the zero-field splitting effect of the Ni^{II} ions is dominant.

Fig. 12 presents the relation M = f(H) for complex **3**. As the magnetic field increase, the M vs H curve indicates linear relation up to 5 T with value of magnetization 1.38 μ_B Magnetization of the sample even at 5 Tesla and 2 K is below the saturation value of 2 μ_B expected for a S = 1 ground state with g = 2 in the absence of zero-field splitting. The shape of the curve formed by the experimental points of **3** does not follow the Brillouin function [52]. The experimental values of magnetizations are lower than the simulated values calculated with the Brillouin function for isolated nickel(II) ion and demonstrate the role played by zero-field splitting effect for the Ni^{II} ions and/or weak intermolecular antiferromagnetic interaction.

4. Conclusions

The size of 3d cation and its coordination preferences are crucial for geometry of trinuclear 3d–4f–3d complex resulting in different relative position of two Schiff base ligands and slightly shorter distances between 3d and 4f ions for Ni^{II}–Ln^{III}–Ni^{II} (where Ln^{III} = La^{III} (1) and Nd^{III} (2)) in comparison to previously reported by us heteronuclear Cu^{II}–Ln^{III}–Cu^{II} (where Ln^{III} = Ce^{III}, Pr^{III} and Nd^{III}) compounds. In presented crystals 1 and 2 the metal centers of nickel(II) and lantadnide(III) ions are bridged by two Schiff base's phenolato oxygens and additionally by the acetate ions.

The magnetic properties obtained for Ni^{II}–La^{III}–Ni^{II} (1) show weak antiferromagnetic exchange coupling between the terminal nickel(II) ions through the diamagnetic lanthanum(III) center. The measurement of variable-temperature magnetic susceptibility reveals antiferromagnetic interaction between spin carriers in the heterotrinuclear complex Ni^{II}–Nd^{III}–Ni^{II} (2). The magnetic data for the mononuclear Ni^{II} (3) compound indicates zero field splitting effect of the Ni^{II} ion.

Appendix A. Supplementary data

CCDC 876079, 876080 and 876081 contains the supplementary crystallographic data for **1**, **2** and **3**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail deposit@ccdc.cam.ac.uk.

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