Research Article

Interactions of Trivalent Lanthanide Cations with a New Hexadentate Di-Schiff Base: New Lanthanide(III) Complexes from \((N\text{E},N'\text{E})-2,2'-(\text{ethane-1,2-diylbis(oxy)})\text{bis}(N-(\text{pyridin-2-ylmethylene})\text{ethanamine})\)

Mantha Tsiouri,1 Konstantina Skorda,2 Christos Papadimitriou,1 Yang Li,3 J. Derek Wollins,3 and John C. Plakatouras1

1 Department of Chemistry, University of Ioannina, 451 10 Ioannina, Greece
2 Faculty of Physics and Chemistry, Hellenic Army Academy, 166 73 Vari, Greece
3 School of Chemistry, University of St. Andrews, North Haugh, St. Andrews, Fife, Scotland, KY16 9ST, UK

Correspondence should be addressed to John C. Plakatouras, iplakatu@cc.uoi.gr

Received 22 April 2010; Accepted 2 May 2010

Academic Editor: Spyros Perlepes

Copyright © 2010 Mantha Tsiouri et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

The novel lanthanide(III) complexes \([\text{Ln(NO}_3\text{)}_2\text{L}](\text{NO}_3\text{)}\cdot3\text{MeOH} (\text{Ln} = \text{La 1, Pr 2})\) and \([\text{Ln(NO}_3\text{)}_3\text{L}](\text{NO}_3\text{)}\cdot2\text{MeOH} (\text{Ln} = \text{Gd 3, Yb 4}),\) where \(\text{L} = (\text{NE},N'E)-2,2'-(\text{ethane-1,2-diylbis(oxy)})\text{bis}(N-(\text{pyridin-2-ylmethylene})\text{ethanamine}),\) have been obtained by direct reaction of the Schiff base ligand and the corresponding hydrated lanthanide(III) nitrates in methanol. All complexes were characterized spectroscopically and thermogravimetrically. Complex 4 was also characterized with crystallographic studies: orthorhombic \(P2_12_12_1, a = 10.6683(14), b = 13.4752(15), c = 19.3320(26) \text{ Å}.\) In the molecular structure of 4, Yb(III) is surrounded by all donor atoms of the Schiff base (four nitrogen and two oxygen atoms) and four oxygen atoms belonging to two bidentate chelating nitrato ligands.

1. Introduction

Schiff base metal complexes have a key role in the development of coordination chemistry, resulting in an enormous number of publications, ranging from pure synthetic work to modern physicochemical and biochemically relevant studies of metal complexes [1].

The lanthanide cations can promote Schiff base condensation and can give access to complexes of otherwise inaccessible ligands. This fact, in combination with the applications of lanthanide macrocyclic complexes emerging from biology and medicine, has boosted research on these areas [2].

One of the major applications of lanthanide complexes in medicine is their use as water proton relaxation agents for NMR imaging [3, 4]. The research in this field is directed towards the synthesis of stable, nontoxic, highly paramagnetic molecules with the ability to improve efficiently the contrast of the magnetic resonance image. The number of coordinated water molecules on the paramagnetic center (usually gadolinium(III)) greatly contributes to the relaxivity (the efficiency with which the complex enhances the proton relaxation rates of water) of the contrast agent. Initially polyaminocarboxylates were utilized as ligands for the preparation of such complexes, with \([\text{Gd(DTPA)}(\text{H}_2\text{O})]^{2-}\) (DTPAH5 = diethylenetriaminepentaacetic acid) being the most commonly used contrast agent. Though the aforementioned agent has a high stability constant, reducing the toxic effect of the free metal ion, its disadvantage is the availability of only one water coordination site.

A large number of articles have been published on lanthanide complexes with the hexadentate Schiff base derived by the condensation of 2,6-diacylpyridine and
ethylendiamine [5–16]. These complexes are stable enough under physiological conditions. However, only recently, research work dealing with the various aspects involving different physicochemical properties and complexation behaviour of tetradentate Schiff bases has appeared in the literature, primarily focusing on the separation of actinides from lanthanides in nuclear reprocessing [17] and catalytic properties [18].

Previously, we have reported the synthesis and the structural and spectroscopic characterization of lanthanide complexes with N,N′-bis[1-(pyridin-2-yl)ethylidene]ethane-1,2-diamine [19] and N,N′-bis(pyridin-2-ylmethylene)benzene-1,2-diamine [20]. It was found that the ethylenediamine "hinge" of the di-Schiff base ligand eliminates the possibility of coplanar coordination of the four nitrogen donors [19] while when we changed the ethylenediamine moiety with 1,2-phenylenediamine to force planar coordination of the tetradentate di-Schiff base, we ended up with the lanthanide cations outside of the four nitrogens plane [20]. In a different work, [21], we found that N,N′-bis(pyridin-2-ylmethylene)cyclohexane-1,2-diamine has an intermediate coordinating behaviour to the lanthanides.

In a previous work, the utilization of 8-hydroxy-quinoline-2-carboxaldehyde for the preparation of Schiff bases leads to products with poor solubility [22]. The next step in our research is to elongate the diamine part of the above-mentioned ligands, incorporating donor atoms, and study the structure and the stability of the prepared complexes. Since the denticity of the ligands is increased, we expected more stable complexes. Herein we report the synthesis and characterization of four new lanthanide complexes with (NE,N′E)-2,2′-(ethane-1,2-diylibis(oxy))bis(N-(pyridin-2-ylmethylene)ethanamine), a ligand derived by the condensation of 2,2′-(ethane-1,2-diylibis(oxy))diethanamine and pyridine-2-carboxaldehyde.

2. Experimental

2.1. Materials and Instrumentation. All manipulations were carried out under aerobic conditions. Metal salts and organic molecules were purchased from Aldrich and used as received. Solvents were of analytical grade (Lab-Scan Chemical Co) and used without further purification. C, H, and N analyses, IR (4000–370 cm⁻¹) and far-IR (600–30 cm⁻¹) [20], and UV/Vis spectra in the solid state [23] and in solution, [24] thermal studies, and room temperature magnetochemical measurements [20] were carried out as previously described.

2.2. Preparation of the Compounds. The ligand (NE,N′E)-2, 2′-(ethane-1,2-diylibis(oxy))bis(N-(pyridin-2-ylmethylene)-ethanamine) was synthesized from the condensation of 2,2′-(ethane-1,2-diylibis(oxy))diethanamine and pyridine-2-carboxaldehyde in situ.

To a stirred solution of pyridine-2-carboxaldehyde (0.40 g, 3.73 mmol) in methanol (15 mL), a solution of 2, 2′-(ethane-1,2-diylibis(oxy))diethanamine (0.27 g, 1.86 mmol) in methanol (5 mL) was added. The resulting yellowish solution was refluxed for 1 hr, and to this the corresponding hydrated lanthanide nitrate (1.86 mmol) in 10 mL of methanol was added. The resulting solutions were heated for a further 30 min and then left undisturbed to evaporate at room temperature, and yielded microcrystalline solids after three days. The solids were isolated by filtration, washed with a small amount of cold methanol (ca. 2 mL) and diethyl ether (2 × 10 mL), and dried under vacuum, over silica gel. The yields were within the range of 55%–65%. A small portion of the mother liquid of complex 4 was layered with diethyl ether to yield a few small colourless blocks, suitable for X-ray structural studies.

| Table 1: Crystal data and structure refinement for 4. |
| Empirical formula | [Yb(NO3)2L]·(NO3)·2MeOH |
| Formula weight | C23H34N7O14Yb |
| Temperature | 93(2) K |
| Wavelength | 0.71069 Å |
| Crystal system, Space group | Orthorhombic, P212121 |
| Unit cell dimensions | a = 10.668(5) Å |
| | b = 13.475(5) Å |
| | c = 19.332(5) Å |
| Volume | 2779.0(18) Å³ |
| Z, Density (calc.) | 4, 1.792 g/cm³ |
| Absorption coefficient | 3.441 mm⁻¹ |
| F(000) | 1492 |
| Crystal size | 0.21 × 0.1 × 0.08 mm³ |
| Completeness to theta = 25.00° | 99.6% |
| Reflections (collected/independent) | 18754/6025 [R(int) = 0.0217] |
| Data/restraints/parameters | 60250/403 |
| Goodness-of-fit on F² | 1.079 |
| Final R indices [I > 2σ(I)] | R₁ = 0.0193, wR₂ = 0.0434 |
| R indices (all data) | R₁ = 0.0198, wR₂ = 0.0437 |
| Absolute structure parameter | 0.599(6) |
| Largest diff. peak and hole | 1.778 and -0.743 eÅ⁻³ |

Solution/restraints/parameters 60250/403/404

Data/restraints/parameters 60250/403/404

Crystal system, Space group Orthorhombic, P2₁2₁2₁

Unit cell dimensions

a = 10.668(5) Å
b = 13.475(5) Å
c = 19.332(5) Å

Volume

2779.0(18) Å³

Z, Density (calc.)

4, 1.792 g/cm³

Absorption coefficient

3.441 mm⁻¹

F(000)

1492

Crystal size

0.21 × 0.1 × 0.08 mm³

Completeness to theta = 25.00°

99.6%

Reflections (collected/independent)

18754/6025 [R(int) = 0.0217]

Data/restraints/parameters

60250/403

Goodness-of-fit on F²

1.079

Final R indices [I > 2σ(I)]

R₁ = 0.0193, wR₂ = 0.0434

R indices (all data)

R₁ = 0.0198, wR₂ = 0.0437

Absolute structure parameter

0.599(6)

Largest diff. peak and hole

1.778 and -0.743 eÅ⁻³
Table 2: Selected bond distances (Å) and angles (°) for \([\text{Yb(NO}_3]_2\text{L}\)(NO\(_3\))·2MeOH (4).

| Bond distances          | Yb(1)–N(2)  | Yb(1)–O(6)  | Yb(1)–O(1)  | Yb(1)–O(2)  |
|-------------------------|-------------|-------------|-------------|-------------|
| Yb(1)–O(4)              | 2.442(2)    | 2.425(2)    | 2.439(2)    | 2.432(2)    |
| Yb(1)–N(3)              | 2.433(3)    | 2.424(2)    | 2.439(2)    | 2.428(2)    |
| Yb(1)–O(7)              | 2.477(2)    | 2.428(2)    | 2.531(3)    | 2.533(3)    |
| Yb(1)–N(4)              | 2.538(2)    | 2.533(3)    | 2.539(3)    | 2.543(2)    |
| Yb(1)–N(6)              | 2.878(2)    | 2.539(3)    | 2.878(2)    | 2.909(3)    |

| Bond angles              | Yb(1)–N(2)  | 2.410(3)    | Yb(1)–O(6)  | 2.424(2)    |
|-------------------------|-------------|-------------|-------------|-------------|
| Yb(1)–O(4)              | 72.51(8)    | 116.04(8)   | 131.78(8)   | 69.55(7)    |
| O(6)–Yb(1)–O(4)         | 116.04(8)   | 140.00(7)   | 76.60(8)    | 69.61(7)    |
| N(2)–Yb(1)–N(3)         | 115.07(8)   | 113.47(7)   | 76.95(8)    | 65.97(8)    |
| O(6)–Yb(1)–O(3)         | 115.07(8)   | 113.47(7)   | 76.95(8)    | 65.97(8)    |
| O(4)–Yb(1)–O(3)         | 115.07(8)   | 113.47(7)   | 76.95(8)    | 65.97(8)    |

Structural characteristics of H-bonds

| D–H ··· A       | d(D–H) | d(H···A) | d(D···A) | <(DHA) |
|-----------------|--------|---------|---------|--------|
| O(12)–H(4S)···O(11) | 1.00(8) | 1.89(8) | 2.828(4) | 156(7) |
| O(13)–H(8S)···O(12)#1 | 0.98(5) | 1.79(5) | 2.758(4) | 170(5) |

Symmetry transformations used to generate equivalent atoms: #1 –x + 2, y – (1/2), –z + (3/2).

of the nitrate], 1020 m [\(\gamma_2(A_1)\) of the nitrate], 637 m [\(\delta(py)\)], 406 w [\(\gamma(py)\)]. \(\mu_{\text{eff}}\) = 3.47 BM at 21°C. TGA/DTA \((N_2, 1 \text{ atm})\): 61°C–92°C (–MeOH, found: 12.01, calcd.: 12.43%, endotherm), 257°C–337°C (decomposition, split exotherm), 547°C (final plateau, Pr\(_6\)O\(_{11}\), found: 21.99, calcd.: 22.01%).

[\(\text{Gd(NO}_3]_2\text{L}\)(NO\(_3\))·2MeOH (3) Anal. Calc. for \(\text{C}_{22}\text{H}_{30}\text{N}_{7}\text{O}_{13}\text{Gd}\): C, 34.86; H, 4.00; N, 12.94. Found: C, 34.87; H, 3.72; N, 13.00%. Selected IR data (cm\(^{-1}\)): 3386 mw [m(O–H)], 3070 w [m(C–H) ar], 1767 m [\(\nu_1 + \nu_4\) of the nitrate], 1642 s [m(C=O)], 1590 ms, 1573 m [ring stretching vibrations], 1488 versus
using TWIN and BASF commands incorporated in SHELX. CCDC 776362 contains the supplementary crystallographic data for this paper. 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; E-mail: deposit@ccdc.cam.ac.uk.

3. Results and Discussion

Complexes 1–4 were prepared by direct reaction of the hydrated lanthanide nitrate salts and the Schiff base ligand starting materials in methanol in 1:1:2 metal to diamine to aldehyde molar ratio. Though it seems that the ligand (Scheme 1) can be prepared by the direct reaction of its constituents (2, 2’-(ethane-1,2-diylbis(oxy))diethanamine and pyridine-2-carboxaldehyde in 1:2 molar ratio), it was impossible to isolate it in a solid form. This is probably due to the relatively long dietheric chain between the Schiff base moieties. Attempts to prepare the 1:2 complexes using larger excess of the ligand parts and different solvents lead to impure products with unidentified formulae.

The crystal structure of complex 4 (Figure 1(a)) consists of cationic complexes [Yb(NO₃)₂L]⁺, nitrate anions, and two methanol molecules per metal ion held together with hydrogen bonds and C–H···π interactions. The Yb(III) atom, being ten coordinated, is surrounded by six oxygen atoms due to the relatively long dietheric chain between the Schiff base ligand.

The coordination polyhedron is much distorted and can be better described, according to Robertson [27], being between a Hoard dodecahedron and a decatetrahedron. (Figure 1(b)).

The Yb–O bond distances span the range 2.424–2.543 Å and they are in good agreement with previously reported values [7, 8, 17–21, 28], taking into account the lanthanide contraction. Though neutral, the etheric oxygen atoms appear to be coordinated to Yb(III) stronger than the nitrates (mean Yb–O nitrate = 2.47 Å, Yb–O ether = 2.43 Å). There are two probable reasons for this behavior: (a) the macrochelate effect, since the ligand contains six sequential donor atoms and (b) the coordination behavior of the nitrato ligands which are both asymetrically chelated. There are no important differences in the coordination characteristics of the nitrato ligands. Additionally, both of the coordinated nitrates are coplanar to Yb(1), as indicated by the Yb(1)–Oₐₙ₉ or Yb(1)–O₈ distances which are all larger than 175°. The mean Yb–N distance is 2.478 Å, being shorter than the corresponding Yb–Npyridine and is in agreement with our previous data [19–21].

The major differences from our previous work on lanthanoid coordination chemistry with Schiff bases rise from the size and the denticity of the ligand. When tetradentate N₄ ligands were used, (Scheme 2(a)) the four nitrogen donor atoms are coplanar and the metal ion lies approximately on the plane formed. There is also space for a nitrato ligand to approach and bind the lanthanide cation. In the present case, the two chelating pyridine Schiff base coordination sites

---

**Scheme 1**: The ligand (NE,N’E)-2,2’-(ethane-1,2-diylbis(oxy))bis(N-(pyridin-2-ylmethylene)ethanamine) (L).

**Scheme 2**: A schematic representation of the coordination of the Schiff base ligands used, to lanthanides. (a) References 18–21, (b) This work.
exist, but their distances have been significantly increased. In addition, between the nitrogen chelating sites are present two more oxygen donor atoms which eventually bind the lanthanide. (Scheme 2(b)) Furthermore, there is no space to accommodate six donor atoms on the same plane about Yb$^{III}$ and this results in the exclusion of the pyridine nitrogen away of the plane formed (max deviation from the mean plane: 0.051 Å) by the two oxygen and the two imino nitrogen atoms. This way the two pyridine rings are pointing up and down of the plane with a dihedral angle of 53.846(5$^\circ$). With the tetradentate Schiff bases being coordinated to lanthanides, there is enough room for three nitrato ligands to coordinate to the metal. Increasing the denticity of the ligand to six, only two nitrato ligands appear in the coordination sphere of the metal. The ionic nitrate interacts with H-bonds with the solvated methanol molecules. Surprisingly, the coordinated nitrates are not involved in hydrogen bonding interactions. This is probably due to their location in cavities with organic surfaces in the crystal.

The room temperature effective magnetic moments of complexes 2, 3, and 4 show little deviation from the Van Vleck theoretical values.

The values of the bonding parameters $\beta$ (nephelauxetic ratio) and $\delta$ (Sinha’s parameter) of the Pr$^{III}$ complex 2 are calculated from the solid state $f$-$f$ spectra by standard equations. Those are 1.003 and $-0.30$, respectively, and they suggest that the interaction between the trivalent lanthanide and the ligands is essentially electrostatic and that there is very small participation of the 4f orbitals in bonding [30].

All complexes behave similarly when heated under nitrogen. Complexes 1 and 2 lose their solvated methanol molecules above its boiling point, while 3 and 4 lose the solvated molecules about methanol’s boiling point. This is an indication of stronger H–bonding in their structures. The intermediates are reasonably stable (up to ca. 280°C) and decompose violently due to the nitrates. The final residues, which are obtained above 490°C, correspond to the sesquioxides except for 2, which corresponds to Pr$_6$O$_{11}$.

Preliminary relaxometric data have shown that 3 is pretty stable in aqueous medium in addition to its increased solubility due to the ionic character. Tailoring, with major goal to increase the stability of lanthanide complexes, of new ligands based on the Schiff base described here and previously [18–22] is in progress.

Acknowledgments

This research was cofunded by the European Union in the framework of the program “Heraklitos” of the “Operational Program for Education and Initial Vocational Training” of the 3rd Community Support Framework of the Hellenic Ministry of Education, funded by 25% from national sources and by 75% from the European Social Fund (ESF).

References

[1] M. A. V. Ribeiro da Silva, M. D. M. C. Ribeiro da Silva, M. J. S. Monte, J. M. Gonçalves, and E. M. R. Fernandes, “Energetics of metal-ligand binding in copper(II) and nickel(II) complexes of two Schiff bases,” Journal of the Chemical Society, Dalton Transactions, no. 7, pp. 1257–1262, 1997.

[2] V. Alexander, “Design and synthesis of macrocyclic ligands and their complexes of lanthanides and actinides,” Chemical Reviews, vol. 95, no. 2, pp. 273–342, 1995.
[3] R. B. Lauffer, “Paramagnetic metal complexes as water proton relaxation agents for NMR imaging: theory and design,” Chemical Reviews, vol. 87, no. 5, pp. 901–927, 1987.

[4] J. Hall, R. Häner, S. Aime et al., “Relaxometric and luminescence behaviour of triaquahexaazamacrocyclic complexes, the gadolinium complex displaying a high relaxivity with a pronounced pH dependence,” New Journal of Chemistry, vol. 22, no. 6, pp. 627–631, 1998.

[5] P. H. Smith, J. R. Brainard, D. E. Morris, G. D. Jarvinen, and R. R. Ryan, “Solution and solid-state characterization of europium and gadolinium Schiff base complexes and assessment of their potential as contrast agents in magnetic resonance imaging,” Journal of the American Chemical Society, vol. 111, no. 19, pp. 7437–7443, 1989.

[6] J. de O. Cabral, M. F. Cabral, W. J. Cummins, M. G. B. Drew, A. Rodgers, and S. M. Nelson, “Hexagonal bipyramidal alkaline earth and lead(II) complexes of a hexa-imine macrocyclic ligand,” Inorganic Chimica Acta, vol. 30, pp. L313–L316, 1978.

[7] J. D. J. Backer-Dirks, C. J. Gray, F. A. Hart, M. B. Hursthouse, and B. C. Schoop, “Preparation and properties of complexes of lanthanides with a hexadentate nitrogen-donor macrocycle: X-ray crystal structure of the complex [La(NO3)3L],” Journal of the Chemical Society, Chemical Communications, no. 7, pp. 1665–1673, 1987.

[8] A. M. Arif, J. D. J. Backer-Dirks, C. J. Gray, F. A. Hart, and M. B. Hursthouse, “Syntheses, X-ray structures, and properties of complexes of macrocyclic hexaamines with lanthanide nitrates,” Journal of the Chemical Society, Dalton Transactions, no. 7, pp. 1127–1132, 1986.

[9] G. Bombieri, F. Benetollo, A. Polo, L. De Cola, D. L. Smailes, and L. M. Vallarino, “Synthesis, characterization, and crystal structure of a hexaaza macrocyclic complex of lutetium(III),” Inorganic Chemistry, vol. 25, no. 8, pp. 1127–1132, 1986.

[10] F. Benetollo, A. Polo, G. Bombieri, K. K. Fonda, and L. M. Vallarino, “X-ray crystal structures and nuclear magnetic resonance spectra of macrocyclic complexes of neodymium(III) and europium(III),” Polyhedron, vol. 9, no. 11, pp. 1411–1422, 1990.

[11] G. Bombieri, F. Benetollo, A. Polo, K. K. Fonda, and L. M. Vallarino, “NMR, luminescence, and X-ray crystallographic studies of the interaction of uncharged N-donor ligands with europium(III) in the macrocyclic complex [Eu(CH3COO)2(C22H26N6)·4H2O],” Polyhedron, vol. 10, no. 12, pp. 1385–1394, 1991.

[12] S. W. A. Bligh, N. Choi, W. J. Cummins, E. G. Evagorou, J. D. Kelly, and M. McPartlin, “Yttrium(III) and lanthanide(III) metal complexes of an 18-membered hexaaza tetraine macrocycle—crystal structure of the gadolinium(III) complex,” Journal of the Chemical Society, Dalton Transactions, no. 23, pp. 3369–3376, 1994.

[13] F. Benetollo, G. Bombieri, K. K. Fonda, and L. M. Vallarino, “Interaction of β-diketones with LaIII, EuIII, and YIII complexes of the six-nitrogen-donor macrocyclic ligand C22H26N6 and crystal structure of [Eu(CH3COO)2(CH3COO)·6H2O],” Polyhedron, vol. 16, no. 11, pp. 1907–1917, 1997.

[14] G. Bombieri, F. Benetollo, A. Polo, L. De Cola, W. T. Hawkins, and L. M. Vallarino, “Synthesis, characterization, and x-ray crystal structure of tris-isooxicynato complexes of the yttrium(III) and europium(III) ions with a six-nitrogen-donor macrocyclic ligand,” Polyhedron, vol. 8, no. 17, pp. 2157–2167, 1989.

[15] K. K. Fonda, D. L. Smailes, L. M. Vallarino et al., “Interaction of neutral and anionic o-donor organic ligands with europium(III) in the macrocyclic complex [Eu(CH3COO)2(C22H26N6)·4H2O] and crystal structure of [Eu(CH3COO)2(C22H26N6)·3(CH3COO)·9H2O]·7H2O,” Polyhedron, vol. 12, no. 5, pp. 549–562, 1993.

[16] S. W. A. Bligh, N. Choi, E. G. Evagorou, M. McPartlin, and K. N. White, “Dimeric yttrium(III) and neodymium(III) macrocyclic complexes: potential catalysts for hydrolysis of double-stranded DNA,” Journal of the Chemical Society, Dalton Transactions, no. 21, pp. 3169–3172, 2001.

[17] M. G. B. Drew, M. R. St. J. Foreman, M. J. Hudson, and K. F. Kennedy, “Structural studies of lanthanide complexes with tetradentate nitrogen ligands,” Inorganica Chimica Acta, vol. 357, no. 14, pp. 4102–4112, 2004.

[18] S. Gourbatsis, J. C. Plakatouras, V. Nastos, and N. Hadjiliadis, “Effect of the intrinsic activity of lanthanide(III) ions on the structure and catalytic properties of chiral Schiff base-lanthanide(III) complexes,” Inorganica Chimica Acta, vol. 349, pp. 6–16, 2003.

[19] S. Kano, H. Nakano, M. Kojima, N. Baba, and K. Nakajima, “An effect of the ion radius of lanthanide(III) ions on the ionic strength and crystal structure of the gadolinium complex displaying a high relaxivity with a pronounced pH dependence,” New Journal of Chemistry, vol. 30, pp. L313–L316, 2006.

[20] M. Tsiouri, J. C. Plakatouras, A. Garoufis, V. Nastos, and N. Hadjiliadis, “Magnetic interactions of trivalent lanthanide cations with tetradentate Schiff bases. Synthesis and characterization of lanthanide(III) complexes with N,N′-bis(pyridin-2-ylmethylene)benzene-1,2-diamine,” Polyhedron, vol. 5, no. 10, pp. 468–471, 1999.

[21] M. Tsiouri, N. Hadjiliadis, T. Arslan, B. M. Kariuki, and J. C. Plakatouras, “Magnetic interactions of trivalent lanthanide cations with tetradentate Schiff bases: new lanthanide(III) complexes from 1(S,2S,N,E,N′E)-N,N′-bis(pyridin-2-ylmethylenecyclohexane-1,2-diamine,” Inorganic Chemistry Communications, vol. 9, no. 4, pp. 429–432, 2006.

[22] T. Arslan, C. Özgür, M. Tsiouri, J. C. Plakatouras, and N. Hadjiliadis, “Magnetic interactions of trivalent lanthanide cations with a hexadentate Schiff base derived from the condensation of ethylenediamine with 8-hydroxyquinoline-2-carboxaldehyde,” Journal of Coordination Chemistry, vol. 60, no. 6, pp. 699–710, 2007.

[23] F. J. Queyraegeens, H. O. Desseyn, S. P. Perlepes, J. C. Plakatouras, B. Bracke, and A. T. H. Lenstra, “Synthesis, spectroscopy and thermal properties of the nickel(II), palladium(II) and copper(II) complexes of bis(aminooalkyl)oxamides (= LH2) including the crystal structure of Cu2L(NO3)2, Transition Metal Chemistry, vol. 16, no. 1, pp. 92–101, 1991.

[24] M. Mylonas, A. Kretzel, J. C. Plakatouras, N. Hadjiliadis, and W. Bal, “The binding of Ni(II) ions to terminally blocked hexapeptides derived from the metal binding -ESHH- motif of histone H2A,” Journal of the Chemical Society, Dalton Transactions, no. 22, pp. 4296–4306, 2002.

[25] A. Altmare, M. C. Burla, M. Camalli et al., “SIR97—a new tool for crystal structure determination and refinement,” Journal of Applied Crystallography, vol. 32, no. 1, pp. 115–119, 1999.

[26] G. M. Sheldrick, SHELX97—Programs for Crystal Structure Analysis (Release 97-2), Institut für Anorganische Chemie der Universität, Göttingen, Germany, 1998.
[27] B. E. Robertson, “Coordination polyhedra with nine and ten atoms,” *Inorganic Chemistry*, vol. 16, no. 11, pp. 2735–2742, 1977.

[28] I. Baxter, S. R. Drake, M. B. Hursthouse et al., “Effect of polyether ligands on stabilities and mass transport properties of a series of gadolinium(III) β-diketonate complexes,” *Inorganic Chemistry*, vol. 34, no. 6, pp. 1384–1394, 1995.

[29] A. B. P. Lever, E. Mantovani, and B. S. Ramaswamy, “Infrared combination frequencies in coordination complexes containing nitrate groups in various coordination environments—probe for metal—nitrate interaction,” *Canadian Journal of Chemistry*, vol. 49, no. 11, pp. 1956–1965, 1971.

[30] R. K. Agarwal, K. Arora, and R. K. Sarin, “Magneto and spectral studies of lanthanide(III) nitrate complexes of 4-vinylpyridine,” *Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry*, vol. 24, no. 5, pp. 735–747, 1994.