

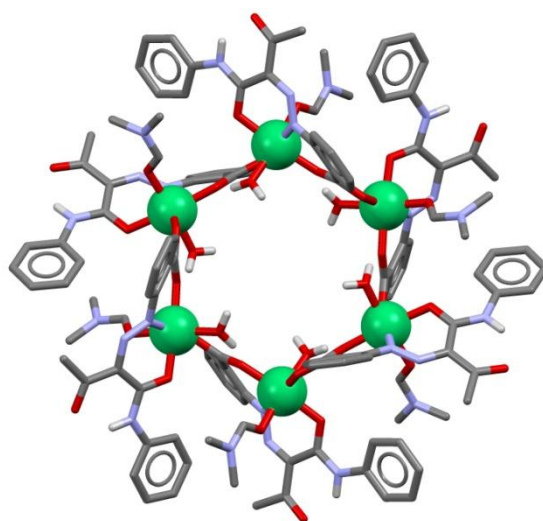
## A CAKE-LIKE HEXANUCLEAR NICKEL(II) COMPLEX DERIVED FROM ARYLHYDRAZONE OF ACETOACETANILIDE

Abel M. Maharramov<sup>1</sup>, Atash V. Gurbanov<sup>1,2</sup>, Namig G. Shikhaliyev<sup>1</sup>,  
Kamran T. Mahmudov<sup>2\*</sup>, Armando J. L. Pombeiro<sup>2\*</sup>

<sup>1</sup>Department of Chemistry, Baku State University, Baku, Azerbaijan

<sup>2</sup>Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa,  
Lisbon, Portugal

### Graphical Abstract



**Abstract.** A hexanuclear nickel(II) complex,  $[\text{Ni}_6(\mu\text{-HL})_6(\text{H}_2\text{O})_6\{(\text{CH}_3)_2\text{NCHO}\}_6]\cdot\text{CH}_3\text{OH}\cdot(\text{CH}_3)_2\text{NCHO}$  (**1**), was obtained upon reaction of  $\text{NiCl}_2$  with (Z)-2-(2-(1,3-dioxo-1-(phenylamino)butan-2-ylidene)hydrazinyl)benzoic acid ( $\text{H}_3\text{L}$ ) in dimethylformamide-methanol mixture (1/20, v/v) at 80 °C. **1** was characterized by IR spectroscopy, elemental and single crystal X-ray diffraction analyses. Within the molecule, the six nickel atoms are united by carboxylate bridges (from six  $\text{HL}^{2-}$ ), forming a cake-like hexagon. Each nickel is surrounded by three oxygen and one nitrogen atoms of  $\text{HL}^{2-}$  and the oxygen atoms of water and dimethylformamide molecules.

**Keywords:** Nickel(II) complex, arylhydrazone of acetoacetanilide, crystal structure.

**Corresponding Authors:** Kamran T. Mahmudov, Armando J.L. Pombeiro, Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisbon, Portugal, Phone: +351 218419237, e-mail: [kamran\\_chem@mail.ru](mailto:kamran_chem@mail.ru), [kamran\\_chem@yahoo.com](mailto:kamran_chem@yahoo.com), [pombeiro@tecnico.ulisboa.pt](mailto:pombeiro@tecnico.ulisboa.pt)

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## 1. Introduction

Polynuclear metal complexes have been attracting intense interest during the last several years. This is due to their relevance to multielectron transfer centres in biological systems, and their unique optical, catalytic and magnetic properties (Balzani

et al., 1996; Blondin & Girerd, 1990; Sierra, 2000; Ambrosi et al., 2008). In order to exploit these properties, it is important to understand their origin and to be able to regulate them through synthetic operations. The fictionalization, synthesis and use of new organic ligands with endogenous bridging and chelating groups are of great significance towards achieving efficient approaches to synthesizing polynuclear metal complexes (Balzani et al., 1996; Blondin & Girerd, 1990; Sierra, 2000; Ambrosi et al., 2008). For instance, carboxylic or sulfonic group(s) functionalized arylhydrazones of active methylene compounds were successfully used in the synthesis of polynuclear Na(I), Cu(II), Zn(II), Cd(II) and Mn(II), as well as heteronuclear Na(I)-Cu(II) and K(I)-Cu(II) complexes (Mahmudov et al., 2013).

On the other hand, polynuclear nickel(II) complexes to have a large single-ion zero-field splitting and ferromagnetic coupling can be synthesized by using multifunctional organic ligands. Polynuclear nickel(II) complexes containing up to four metal ions are not rare, but assemblies with five, six and more nickel(II) ions still remain a matter of curiosity (Paine et al., 2003; Biswas et al., 2009). In this paper we report a cake-like hexanuclear nickel(II) complex,  $[\text{Ni}_6(\mu\text{-HL})_6(\text{H}_2\text{O})_6\{(\text{CH}_3)_2\text{NCHO}\}_6]\cdot\text{CH}_3\text{OH}\cdot(\text{CH}_3)_2\text{NCHO}$  (**1**), which is obtained by reaction of  $\text{NiCl}_2$  with (*Z*)-2-(2-(1,3-dioxo-1-(phenylamino)butan-2-ylidene)hydrazinyl)benzoic acid ( $\text{H}_3\text{L}$ ) in dimethylformamide-methanol mixture (1/10, v/v) at  $80^\circ\text{C}$ <sup>1</sup>.

## 2. Results and Discussion

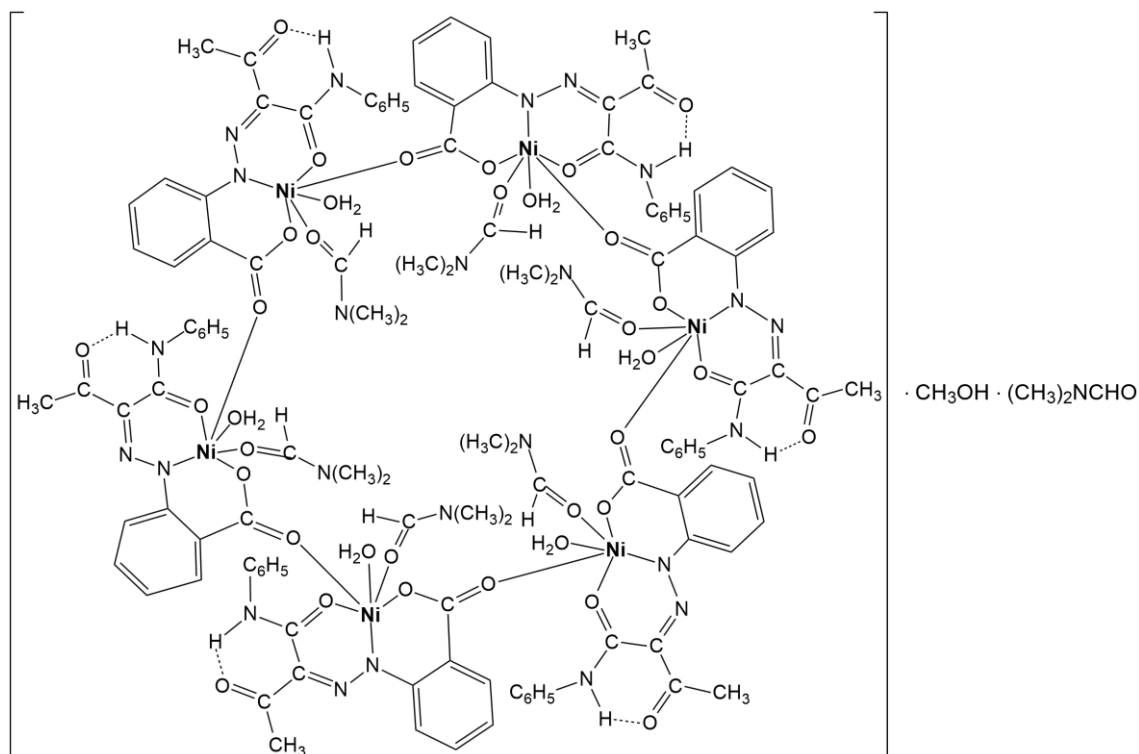
The reaction of  $\text{NiCl}_2$  with  $\text{H}_3\text{L}$  in the presence of  $\text{N}(\text{C}_2\text{H}_5)_3$ , in dimethylformamide-methanol mixture (1/20, v/v) at  $80^\circ\text{C}$  yields  $[\text{Ni}_6(\mu\text{-HL})_6(\text{H}_2\text{O})_6\{(\text{CH}_3)_2\text{NCHO}\}_6]\cdot\text{CH}_3\text{OH}\cdot(\text{CH}_3)_2\text{NCHO}$  (**1**) (Scheme 1)<sup>1</sup>. **1** has been isolated as an air-stable crystalline solid and characterized by IR spectroscopy, elemental analysis and X-ray crystallography. The IR spectrum of **1** displays 3394 (br.)  $\nu(\text{H}_2\text{O})$ , 2930  $\nu(\text{NH})$ , 1665  $\nu(\text{C}=\text{O})$ , 1542  $\nu(\text{C}=\text{N})$  lines, the peaks being significantly shifted in relation to those of the spectrum of the free ligand (3436 (br.)  $\nu(\text{H}_2\text{O})$ , 3240  $\nu(\text{NH})$ , 1696 and 1663  $\nu(\text{C}=\text{O})$ , 1599  $\nu(\text{C}=\text{N})$ ) (Gurbanov et al., 2017). Elemental<sup>1</sup> and X-ray analysis (see below)<sup>2</sup> support the proposed formulation of **1** as a hexamer<sup>2</sup>.

In the hexanuclear complex **1** (Fig.1) each nickel ion has a distorted octahedral coordination geometry with strong bonds in the equatorial plane and weak bonds in axial positions. The  $(\text{HL})^{2-}$  ligand coordinates the  $\text{Ni}^{\text{II}}$  ion in the equatorial plane *via* the carboxylate oxygen O2 and the carbonyl oxygen O1 and the deprotonated N3 of the

<sup>1</sup> 0.325 g (1.0 mmol) of  $\text{H}_3\text{L}$  was dissolved in 10 mL dimethylformamide-methanol mixture (1/20, v/v), then 0.130 g (1.0 mmol) of  $\text{NiCl}_2$  and 0.10 mL  $\text{N}(\text{C}_2\text{H}_5)_3$  were added. The mixture was stirred and heated to  $80^\circ\text{C}$  for 30 min and then left at room temperature for slow evaporation; green crystals of **1** suitable for X-rays started to form after *ca.* 5 d. Yield 39 % based on  $\text{NiCl}_2$ . Anal. Calcd for  $\text{C}_{124}\text{H}_{143}\text{N}_{25}\text{Ni}_6\text{O}_{38}$  ( $M = 2943.61$ ): C, 50.59; H, 4.90; N, 11.90. Found: C, 50.37; H, 4.84; N, 11.88 %. IR (KBr): 3394 (br.)  $\nu(\text{H}_2\text{O})$ , 2930  $\nu(\text{NH})$ , 1665  $\nu(\text{C}=\text{O})$ , 1542  $\nu(\text{C}=\text{N})$   $\text{cm}^{-1}$ .

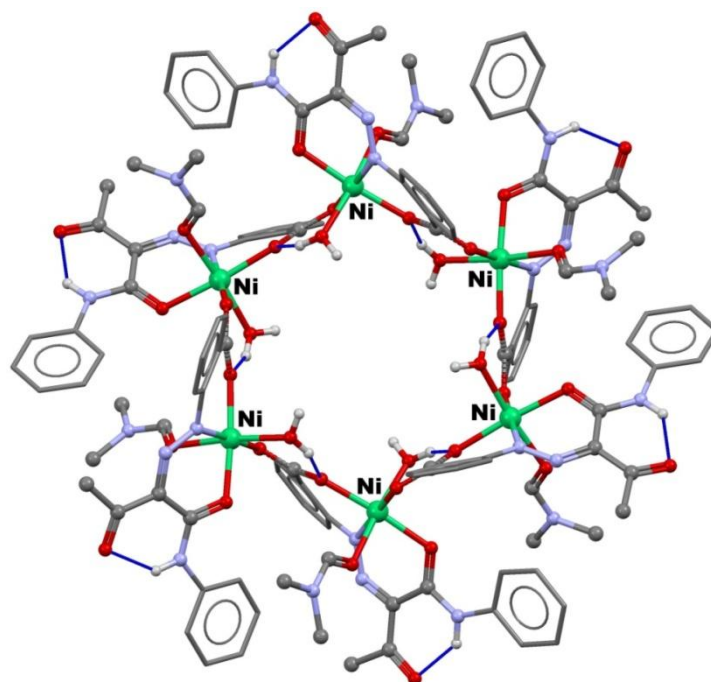
<sup>2</sup> Crystal data for compound **1** ( $\text{C}_{124}\text{H}_{143}\text{N}_{25}\text{Ni}_6\text{O}_{38}$ ):  $M_r = 2943.61$ , MoK $\alpha$  radiation,  $\lambda = 0.71073$  Å, trigonal space group, *R*-1,  $a = 28.6059(15)$ ,  $b = 28.6059(15)$ ,  $c = 16.6749(10)$  Å,  $\alpha = 90$ ,  $\beta = 90$ ,  $\gamma = 120$ ,  $Z = 3$ ,  $V = 11816.9(14)$  Å<sup>3</sup>,  $T = 296$  K,  $\rho_{\text{calcd}} = 1.192$   $\text{Mg m}^{-3}$ ,  $F(000) = 4392$ ,  $\mu = 0.775$   $\text{mm}^{-1}$ ,  $R1 = 0.0394$ ,  $wR2 = 0.0877$  and  $\text{GOF} = 1.011$ . CCDC-1587318 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

hydrazone moiety at distances of 1.996(2), 2.0049(19) and 1.995(2) Å, respectively. The equatorial plane is completed by an oxygen atom O3 of the carboxylate group from a neighboring molecule at 2.0556(18) Å. The axial sites are occupied by a water molecule with O4 at 2.098(2) Å, and a dimethylformamide molecule with O5 at 2.092(2) Å. As reported in a hexanuclear nickel(II) silsesquioxane (Bilyachenko et al., 2016), C–H···O and C–H··· $\pi$  types of inter- and intramolecular noncovalent interactions were found in **1**. It also presents intramolecular hydrogen bond involving the NH groups that donate to O<sub>keto</sub> atoms.



**Scheme 1.** Schematic representation of **1**

In summary, we have synthesized and fully characterized the first cake-like hexanuclear nickel complex with an arylhydrazone of  $\beta$ -diketone ligand. The application of complex **1** in catalysis and the preparation of other polynuclear metal complexes of arylhydrazone ligands are in progress.



**Fig. 1.** Molecular structure of **1**. Hydrogen atoms and solvent molecules were omitted for clarity

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