A ladder-type coordination polymer constructed from two different macrocyclic building units – a calix[4]arene tetracarboxylate and a hexaazamacrocyclic nickel(II) complex

Lyudmila V. Tsymbal, Yaroslaw D. Lampeka, Vyacheslaw I. Boyko, Vitaly I. Kalchenko,
Svitlana V. Shishkina and Oleg V. Shishkin

Electronic Supplementary Information

Experimental

General remarks

All commercially available chemicals were of reagent grade and were used as received. Elemental analysis (Carlo Erba C,H,N analyzer), IR spectroscopy (Perkin-Elmer Fourier-transform spectrometer, samples in KBr pellets), diffuse reflectance spectra (Specord 210 spectrophotometer, Analytik Jena SE), diffractometric measurements (Bruker D8 diffractometer, CuKα radiation λ = 1.54178 Å), and thermogravimetric analysis (Paulic, Paulic and Erdey derivatograph) were used to study the composition and properties of the products obtained. The luminescent spectra of the solid samples at room temperature were recorded on a luminescent Perkin-Elmer LS-55 spectrograph with laser excitation at 275 nm.

Syntheses

The nickel(II) complex (3,10-dimethyl-1,3,5,8,10,12-hexaazacyclotetradecane)nickel(II) diperchlorate $[NiL](ClO_4)_2$ (**1**) was prepared *via* template condensation of bis(ethylenediamine) nickel(II) perchlorate with methylamine and formaldehyde as described in the literature [1]. 5,11,17,23-tetrakis(*tert*-butyl)-25,26,27,28-tetrakis(carboxymethoxy)calix[4]arene, H_4CCA, was synthesized by hydrolysis of the corresponding calix[4]arene tetraester [2]. The coordination polymer $\{[(NiL)_3(HCCA)_2]\cdot 9DMF\cdot H_2O\}_n$ (**2**) was prepared by liquid–liquid diffusion method as follows.

The solution of $[NiL](ClO_4)_2$ (0.1 mmol) in 3 mL water/DMF mixture (1/2 by volume) was layered with the solution of H_4CCA (0.1 mmol) in DMF (2 mL) and the reaction mixture was allowed to stand overnight at room temperature. The light pink crystals formed were filtered off, washed with water and dried in air. The yield is 45% (based on Ni).

$\{[(NiL)_3(HCCA)_2]\cdot 9DMF\cdot H_2O\}_n$ (**2**), $C_{161}H_{264}N_{27}Ni_3O_{34}$ (3298.10): calcd C 58.63, H 8.07, N 11.47; found C 58.4, H 8.2, N 11.3.

Single crystals suitable for X-ray diffraction analysis were selected from the samples resulted from syntheses.

The reduction of the intensity of a strong band of protonated carboxylic groups at ca. 1745 cm^{-1} and the appearance of two moderately strong bands at 1655 and 1618 cm^{-1} characteristic of coordinated carboxylate in the IR spectrum of **2** as compared to H_4CCA are in accordance with the coordination mode of the calix[4]arene ligand (see Fig. S2 below).

Thermal gravimetric analysis of **2** showed a weight loss of 21.3% in temperature range 25 – 120 °C due to the removal of solvent molecules (calculated value 20.5%). No further weight loss was observed up to 200 °C. After that, the weight dropped rapidly with increasing temperature, indicating a decomposition of the complex.

X-ray crystallography

Crystallographic measurements were carried out on a «Xcalibur-3» diffractometer (graphite monochromated MoK$_\alpha$ radiation, CCD detector, ω-scaning).

The structures were solved by direct method using SHELXTL package [3]. The restrictions on the bond lengths in the solvate molecules and the disordered *tert*-butyl fragment in **2** were applied (C_{sp3}-C_{sp3} 1.54 Å, C_{sp3}-N 1.46 Å, C_{sp2}-N 1.36 Å, C_{sp2}=O 1.210 Å). Position of the hydrogen atoms were located from electron density difference maps and refined by "riding" model with $U_{iso} = nU_{eq}$ of the carrier atom (n = 1.5 for methyl and hydroxyl groups and for water molecule and n = 1.2 for other hydrogen atoms). The hydrogen atoms of the NH-groups taking part in the formation of the intermolecular hydrogen bonds are refined in isotropic approximation in the structure **1**. Full-matrix least-squares refinement of the structures against F^2 in anisotropic approximation for the non-hydrogen atoms using 3872 (**1**), 15046 (**2**) reflections was converged to: $wR_2 = 0.096$ ($R_1 = 0.036$ for 2985 reflections with $F>4\sigma(F)$, S = 0.992) for structure **1** and $wR_2 = 0.234$ ($R_1 = 0.077$ for 10134 reflections with $F>4\sigma(F)$, S = 0.999) for structure **2**. The final atomic coordinates, and crystallographic data for complexes **1** and **2** have been deposited to with the Cambridge Crystallographic Data Centre, 12 Union Road, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk) and are available on request quoting the deposition numbers CCDC 933480 for **1** and CCDC 933481 for **2**).

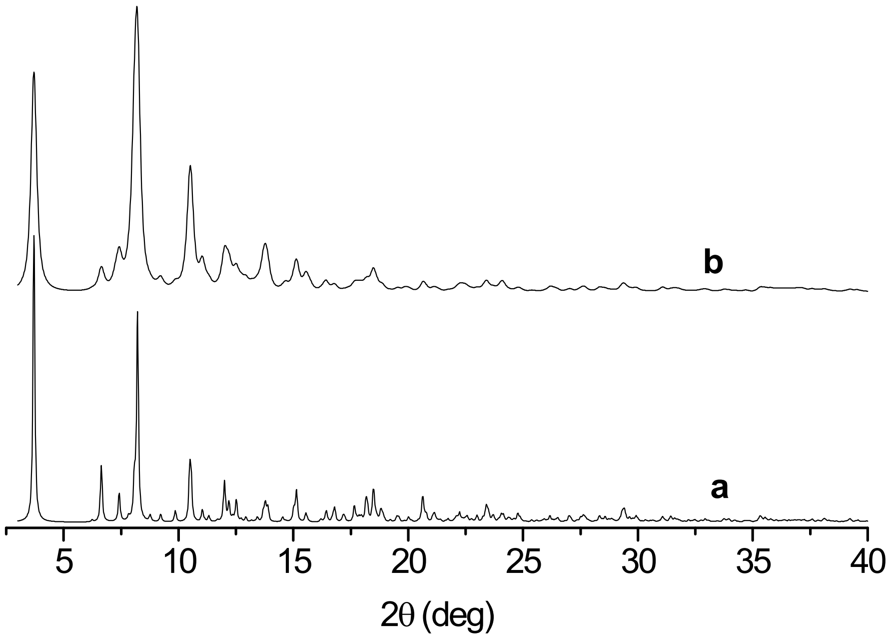


Fig. S1 The X-ray powder diffraction pattern of **2** calculated using the single crystal X-ray data (a) and measured for the polycrystalline sample (b).

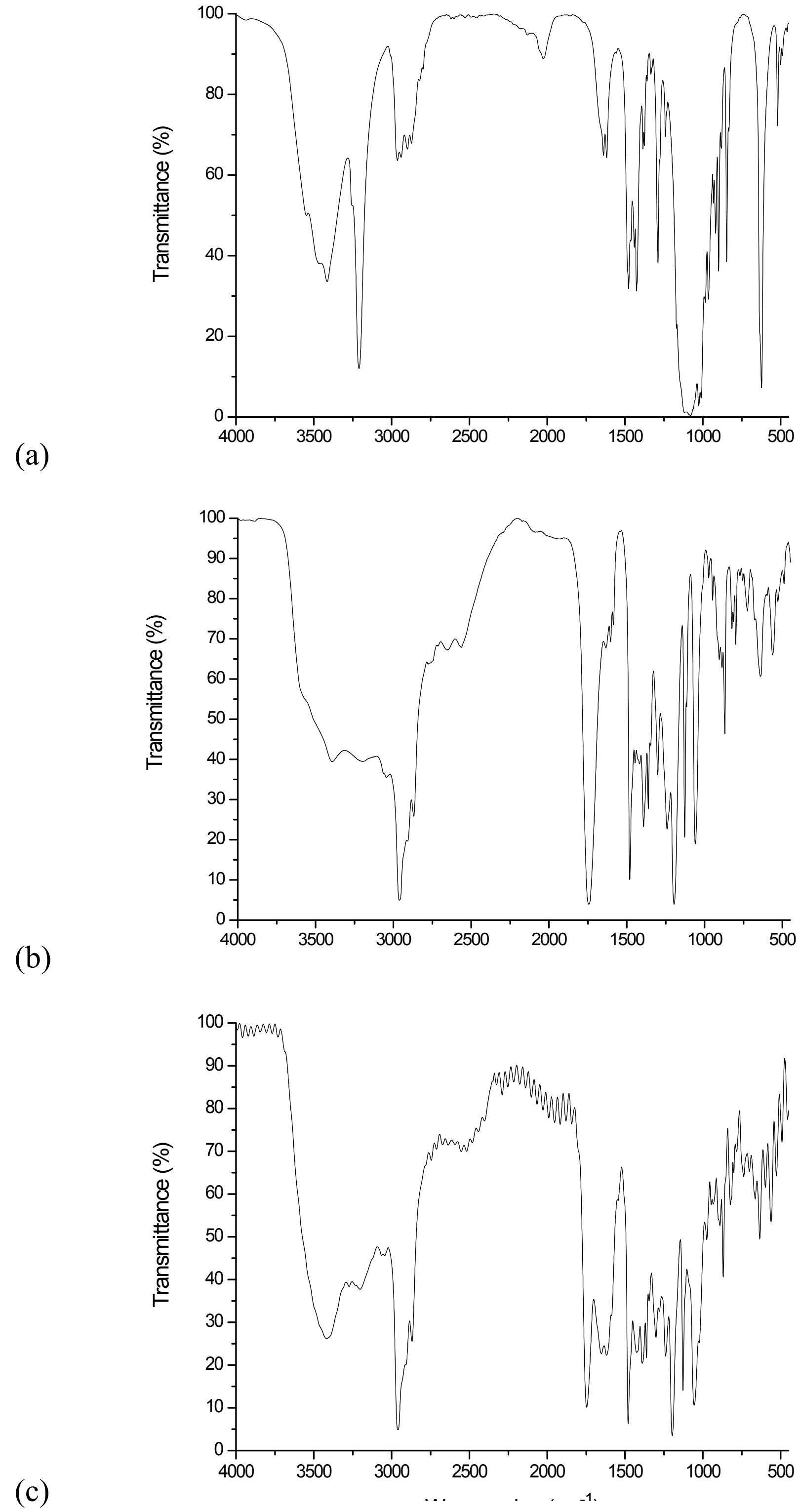


Fig. S2 The IR Spectra of the compounds **1** (a), H_4CCA (b) and **2** (c).

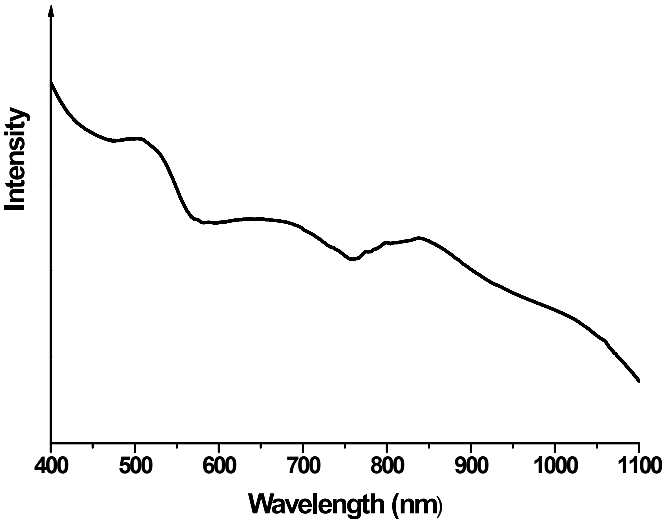
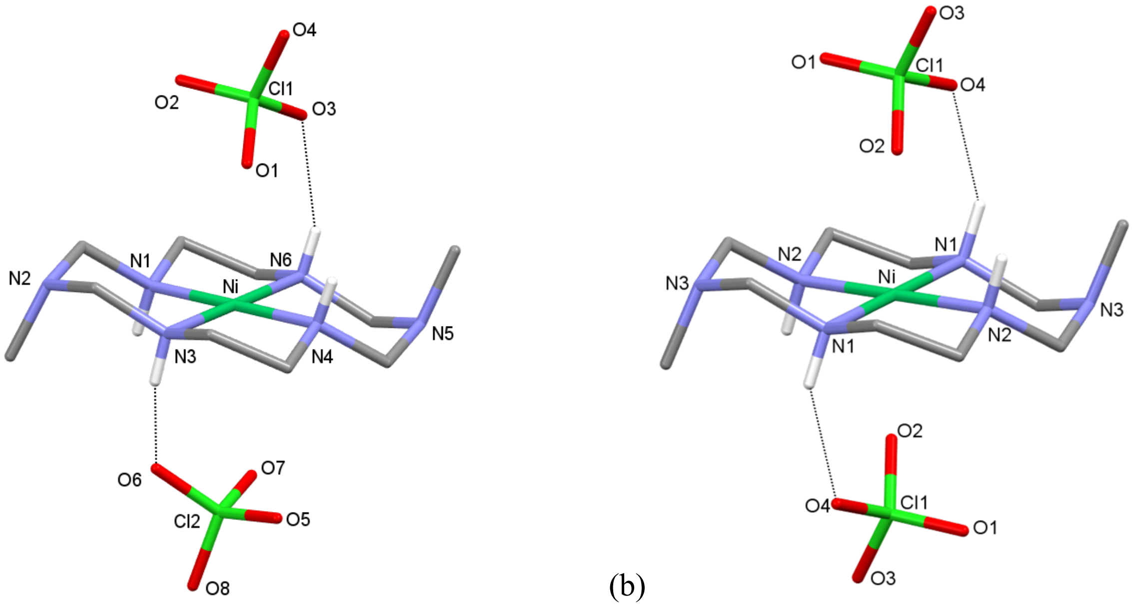


Fig. S3 The solid-state reflectance spectrum of **2**.

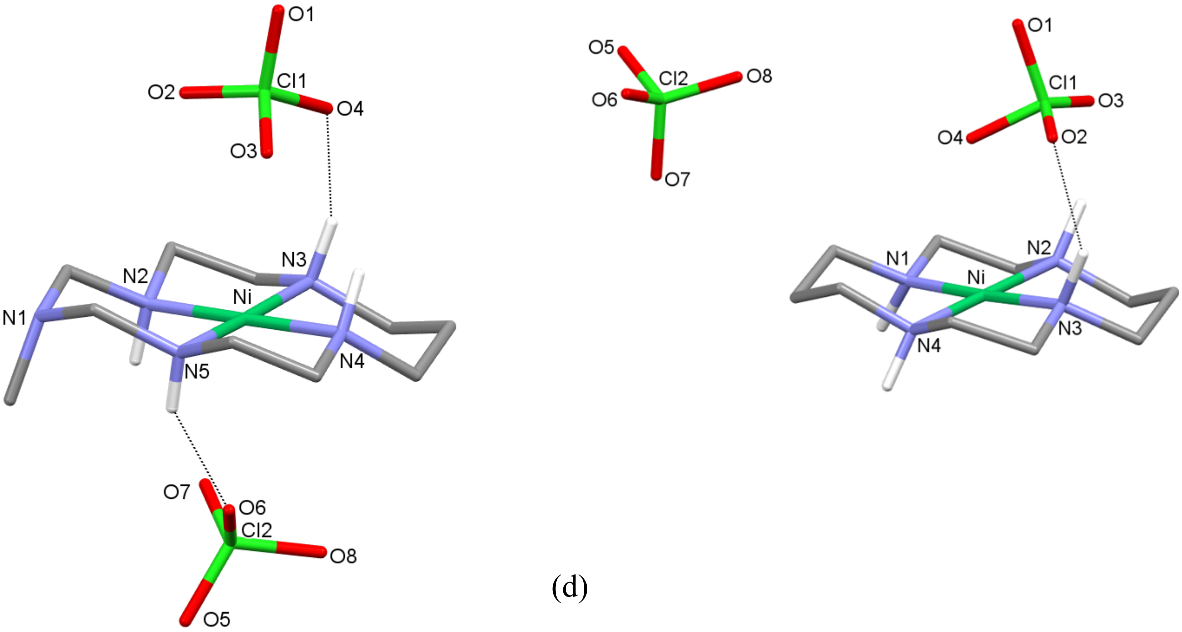


(a)

(b)

D-H...A	d(D...A)	d(H...A)	∠(DHA)
N(6)-H...O(3)	2.987(3)	2.19(3)	156(2)
N(3)-H...O(6)	3.025(3)	2.25(4)	143(3)

D-H...A	d(D...A)	d(H...A)	∠(DHA)
N(1)-H...O(4)	3.075	2.21	149



(c)

(d)

D-H...A	d(D...A)	d(H...A)	∠(DHA)
N(5)-H...O(6)	2.925	2.11	146
N(3)-H...O(4)	3.057	2.12	153

D-H...A	d(D...A)	d(H...A)	∠(DHA)
N(3)-H...O(2)	3.060	2.15	140

Fig. S4 Capped sticks representation of the hydrogen bonds (dotted lines, distances d (Å) and angles ∠ (°) are presented in tables) in the perchlorate salts of the nickel(II) complexes with macrocyclic ligands L (a – this work, b – ref [4]), L^A – ref. [5] (c) and L^B – ref. [6] (d).

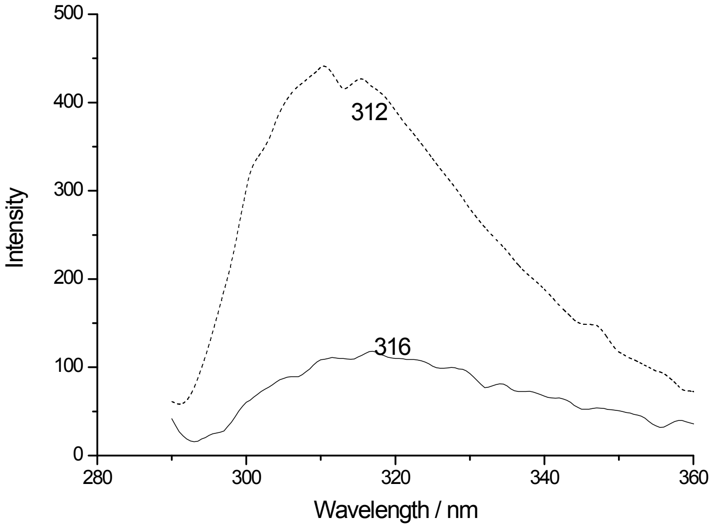
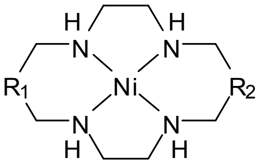


Fig. S5 The solid-state fluorescent emission spectra for **2** (solid lines) and H_4CCA (dotted line, arbitrary intensity scale).

Table S1 Crystallographic parameters, selected interatomic distances (Å) and angles (°) for the perchlorate salts of the nickel(II) complexes of the azamacrocyclic ligands

Compound	**1**	[NiL](ClO$_4$)$_2$	[NiL^A](ClO$_4$)$_2$	[NiL^B](ClO$_4$)$_2$
CCDC code and reference	933480 [this work]	AJEGAY [4]	JOGCUD [5]	FISKEX [6]
Space group	monoclinic, P2$_1$/c	monoclinic, P2$_1$/n	orthorhombic, P2$_1$2$_1$2$_1$	monoclinic, P2$_1$/n
Cell lengths (Å)	a=16.3018(5) b=8.6598(2) c=13.5660(4)	a=8.536(5) b=8.730(5) c=12.736(7)	a=15.967(3) b=13.497(3) c=8.737(2)	a=9.596(2) b=13.887(6) c=13.137(3)
Cell angles (°)	α=γ=90 β=112.177(4)	α=γ=90 β=102.45(1)	α=β=γ=90	α=γ=90 β=90.78(2)
Cell volume (Å^3); Z	1773.44(9); 4	926.8; 2	1882.9; 4	1750.5; 4
Average Ni-N distance (Å)	1.933(2)	2.009	1.932	1.954
Shortest Ni-O distance (Å)	2.886(2) (O1)	2.681 (O2)	3.182 (O3)	2.931 (O4)
Average ∠N-Ni-N in 5-membered chelate rings (°)	87.1(1)	86.3	86.5	86.0
Average ∠N-Ni-N in 6-membered chelate rings (°)	92.9(1)	93.7	93.6	94.0
Average ∠C-N-C at distal nitrogen atoms (°)	114.0(1)	114.9	115.0	-
Packing index calculated by PLATON [7] (%)	75.3	73.2		

The structures of the nickel(II) macrocyclic cation: L = 3,10-dimethyl-1,3,5,8,10,12-hexaazacyclotetradecane, L^A = 3-methyl-1,3,5,8,12-pentaazacyclotetradecane and L^B = 1,5,8,12-tetraazacyclotetradecane (cyclam)



R$_1$ = R$_2$ = N-CH$_3$ [NiL]$^{2+}$

R$_1$ = CH$_2$ R$_2$ = N-CH$_3$ [NiL^A]$^{2+}$

R$_1$ = R$_2$ = CH$_2$ [NiL^B]$^{2+}$

Table S2 Selected interatomic distances (Å) and angles (°) for **1** and **2**

1		**2**	
Ni-N1	1.933(2)	Ni1-N1	2.070(3)
Ni-N3	1.935(2)	Ni1-N3	2.027(4)
Ni-N4	1.933(2)	Ni1-N4	2.046(4)
Ni-N6	1.932(2)	Ni1-N6	2.062(4)
		Ni1-O7	2.093(3)
		Ni1-O11	2.159(2)
		Ni2-N7	2.059(3)
		Ni2-N8	2.059(3)
		Ni2-O4	2.101(2)
N1-Ni-N3	92.86(8)	N1-Ni1-N3	95.74(15)
N1-Ni-N6	87.04(8)	N1-Ni1-N6	83.90(14)
N3-Ni-N4	87.14(8)	N3-Ni1-N4	86.28(15)
N4-Ni-N6	92.96(8)	N4-Ni1-N6	93.99(15)
		N7-Ni2-N8	86.38(12)
		N7-Ni2-N8*	93.62(12)

Symmetry transformations used to generate equivalent atoms: * 1-x, 1-y, 1-z.

Table S3 Parameters of the hydrogen bonds in **2**.

D-H...A	d(H...A)	d(D...A)	∠(DHA)
N(1)-H...O(12)	2.09	2.907(5)	146
N(4)-H...O(6)	2.20	3.023(3)	146
N(7)-H...O(3)	2.20	3.035(4)	150
N(3)-H...O(1SC)	2.14	2.953(3)	146
N(6)-H...O(1SB)	2.20	3.025(3)	147
N(8)-H…O(9)	2.36	3.095(3)	136
O(10)-H...O(2)	2.33	2.855(2)	121
O(10)-H...O(5)	2.30	2.811(3)	120
O(10)-H...O(8)	2.12	2.632(2)	120
O(1W)-H…O(6)	1.76	2.635(8)	177
O(1W)-H…O(1SD)	2.10	2.99(1)	177

* Hydrogen bond with oxygen atom of a DMF molecule.

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