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

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The crystal structures of a new type of coordination polymer formed by the high-spin form of a hexaazamacrocyclic nickel(II) complex and a lower rim calix[4]arene tetracarboxylate trianion (2) as well as the perchlorate salt of the low-spin form of this macrocyclic cation (1) are reported. The porosity of the network is characterized by the presence of polar and non-polar voids formed by carboxylate substituents/azamacrocyclic cations and aromatic/*tert*-butyl substituents of the calix[4]arene, respectively.

Porous crystalline materials of coordination polymeric nature (porous coordination polymers, PCPs) which are formed *via* donor–acceptor bonds between the metal centres (nodes) and the linkers (bridging organic ligands) have attracted growing attention during the past decade due to the high tunability of their structural characteristics and their potential applications in different areas including separation, gas storage and catalysis.<sup>1</sup> Due to their very high inherent thermodynamic stability and kinetic inertness<sup>2</sup> transition metal complexes of tetradentate azamacrocycles represent a class of opportune nodes for the construction of coordination polymers (CPs) since they retain integrity during the formation of polymeric chains and possess predictable linear binodality caused by the presence of two *trans*-apical positions accessible for interaction

of the metal ion with the bridging ligands. To date, a number of CPs based on azamacrocyclic complexes have been described; among them, simple aromatic polycarboxylates are the most popular linkers.<sup>3</sup> Usually, these linkers play an architectural role in the spatial organization of metal-containing units in polymeric networks without the involvement of their intrinsic properties in the functional behaviour of the materials. In our opinion, using more sophisticated ligands will allow the introduction of new colours into the palette of properties of PCPs, and a calixarene platform bearing carboxylate groups seems to be a very promising candidate.

Calixarenes represent a fascinating class of macrocyclic molecules which have been extensively used in supramolecular chemistry. This has resulted from their synthetic availability coupled with the presence of cavities capable of binding cationic, anionic or neutral guests.<sup>4</sup> Conformational flexibility displayed by such compounds (*e.g.*, *cone*, *partial cone*, *1,3-* or *1,2-alternate* for particular cases of calix[4]arenes) opens wide possibilities for the construction of supramolecular aggregates of different morphologies. Thus, PCPs containing a calixarene-based linker could represent a new type of material possessing two-level porosity associated both with the ligand itself and with the framework.<sup>5</sup>

To date, the construction of CPs of a given type has been focused mainly on upper-rim substituted calixarenes bearing different coordinating fragments.<sup>6</sup> Among them, *p*-sulfonated calixarenes are the most widely studied.<sup>7</sup> At the same time, there have been only a few reports on CPs of calix[4]arene-based polycarboxylates, namely upper- or lower-rim 1,3-disubstituted as well as tetrasubstituted derivatives.<sup>5,8–12</sup>

Both *cone*<sup>5,8</sup> and *1,3-alternate*<sup>9</sup> conformations of the 1,3-disubstituted calix[4]arene linker have been found in 1D,<sup>8</sup> 2D (ref. 5, 8) or 3D (ref. 9) CPs formed by solvated M<sup>2+</sup> ions (M = Co, Cu, Zn, Cd). In contrast, only 1D structures have been recognized for CPs based on tetracarboxylic calix[4]arenes, irrespective of whether they are in *1,3-alternate*<sup>10,11</sup> or *cone*<sup>12</sup> conformation. Notably, the calix[4]arene units in all these CPs

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represent endomolecular complexes with a metal cation (usually  $\text{Na}^+$ ) residing in the coordination pocket formed by the ether and carbonyl oxygen atoms of pendant groups; the interconnection of such endocomplexes into coordination networks is realized *via* exo-coordination of other metallic centers ( $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ag}^+$ ) to the carboxylic groups. Interestingly, the only complex of a tetracarboxyl calix[4]arene anion with an azamacrocyclic cation also contains a sodium ion endocoordinated by three carboxylates, while the fourth one occupies the apical position in the coordination sphere of copper(II), thus resulting in a non-polymeric structure.<sup>13</sup>

In the present contribution we report, to the best of our knowledge, the first example of a polymeric coordination network composed of a calixarene carboxylate and a transition metal azamacrocyclic complex, *i.e.*, the trianion of lower-rim appended calix[4]arene tetracarboxylic acid ( $\text{H}_4\text{CCA}$ ) and the high-spin hexaazamacrocyclic (3,10-dimethyl-1,3,5,8,10,12-hexaazacyclotetradecane)nickel(II) cation  $[\text{NiL}]^{2+}$  (Fig. 1). For comparative purposes, the structure of the low-spin macrocyclic precursor  $[\text{NiL}](\text{ClO}_4)_2$  is also discussed.

The starting nickel(II) complex  $[\text{NiL}](\text{ClO}_4)_2$  (**1**) was prepared *via* template condensation of bis(ethylenediamine)nickel(II) perchlorate with methylamine and formaldehyde as described previously.<sup>14</sup> The interaction of **1** with  $\text{H}_4\text{CCA}$  in a DMF-water mixture results in the formation of the product  $\{([\text{NiL}]_3(\text{HCCA})_2] \cdot 9\text{DMF} \cdot \text{H}_2\text{O}\}_n$  (**2**) (for experimental details see ESI†). As observed from the X-ray powder diffraction data, this solid is produced as a pure crystalline phase (Fig. S1, ESI†) identical with the single crystalline sample (*vide infra*). The IR spectrum of **2** displays the main features of  $[\text{NiL}]^{2+}$  and  $\text{H}_4\text{CCA}$  and is in accordance with the composition of the complex and with the coordination mode of the calix[4]arene ligand (Fig. S2, ESI†). Hexa-coordination of the nickel(II) ions in **2** is confirmed by the presence of a number of bands in the solid-state reflectance spectrum (Fig. S3, ESI†) which is typical for a high-spin nickel(II) ion in a tetragonal  $\text{N}_4\text{O}_2$  environment.<sup>2</sup>

The single-crystal X-ray study revealed the ionic nature of **1**†. The asymmetric unit of this complex (Fig. 2a) consists

of a non-centrosymmetric macrocyclic cation and two perchlorate anions forming weak hydrogen bonds with the secondary amino groups of the macrocycle (for the parameters of the hydrogen bonds see Fig. S4, ESI†). The metal ion, possessing a tetragonal  $\text{NiN}_4$  chromophore, is four-coordinated and the lack of donor-acceptor interactions between the metal cation and perchlorate anions is confirmed by the long  $\text{Ni} \cdots \text{O}-\text{ClO}_3$  distances (the shortest  $\text{Ni} \cdots \text{O1}$  contact is 2.886(2) Å). In general, the structure of **1** is similar to those of the nickel(II) complexes with parent macrocyclic ligands, *i.e.* 3-methyl-1,3,5,8,12-pentaazacyclotetradecane<sup>15</sup> and 1,5,8,12-tetraazacyclotetradecane (cyclam),<sup>16</sup> as well as to another polymorph of  $[\text{NiL}](\text{ClO}_4)_2$  which has been briefly described recently<sup>17</sup> (for the values of selected interatomic distances and angles for these complexes see Table S1, ESI†). All four complexes are non-isomorphous and this feature could apparently be explained by subtle differences in hydrogen bonds between the cations and anions in the crystals (Fig. S4, ESI†).

Based on single crystal X-ray diffraction analysis,§ the asymmetric unit of **2** contains one calix[4]arene trianion and two crystallographically independent nickel(II) macrocyclic cations (Fig. 2b), one of which (Ni2) lies on an inversion centre. Both metal ions have a similar tetragonal-bipyramidal  $\text{N}_4\text{O}_2$  environment formed by four equatorial secondary amine donors of the macrocycles and two *trans*-axial oxygen atoms of the carboxylate anions. The coordinative nickel(II)-carboxylate interactions are reinforced by hydrogen bonds between the non-coordinated oxygen atom of the carboxylate group and secondary nitrogen atoms of the macrocycle (Fig. 2b; for parameters of the hydrogen bonds in **2** see Table S3, ESI†).

The coordinated macrocyclic ligand in both **1** and **2** adopts the most energetically favourable *trans*-III (*R,R,S,S*)<sup>18</sup> form with the 5- and 6-membered chelate rings in *gauche* and *chair* conformations, respectively. The methyl substituents at the distal nitrogen atoms in the 6-membered chelate rings are axially oriented. Therewith, the  $\angle \text{C}-\text{N}_{\text{distal}}-\text{C}$  angles in **1** and **2** (*ca.* 115°) are larger than the canonical value for an  $\text{sp}^3$ -hybridized nitrogen atom (109°), thus indicating their partial  $\text{sp}^2$  character as observed in other complexes of this type (Table S1, ESI†).

The main difference between the nickel(II) chromophores in **1** and **2** lies in the Ni-N bond distances. The Ni-N bond lengths in **1** (averaged value: 1.933(2) Å) are essentially shorter than those in **2** (average: 2.055(3) Å). Both fall in the range typical of the complexes with 14-membered tetradentate azamacrocycles with the square-planar low-spin  $\text{NiN}_4$ - and high-spin *trans*- $\text{N}_4\text{O}_2$  chromophores, respectively.<sup>2,19</sup> The arrangement of the nitrogen donor atoms in **1** and those surrounding the Ni1 cation of **2** is nearly coplanar (r.m.s. 0.002 and 0.006 Å, respectively). In the latter case the metal ion is shifted by 0.042 Å to the axial O11 atom (*i.e.*, to the atom forming the *weaker* Ni-O coordination bond). Because of symmetry requirements, the Ni2 $\text{N}_4$  chromophore is strictly coplanar. The elongation of the equatorial Ni-N bonds in **2** as compared to **1** causes the reduction of the bite angles in the 5-membered chelate rings (*cf.* average values: 87.1(1)° and

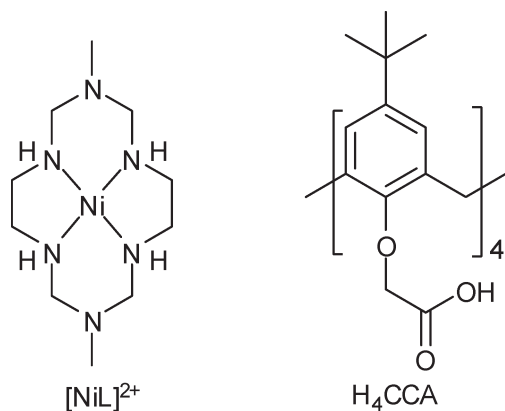
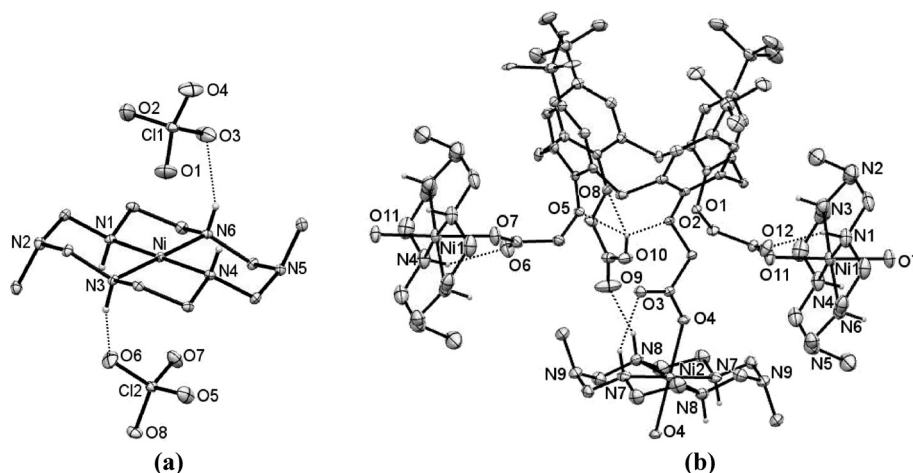


Fig. 1 The structures of the 3,10-dimethyl-1,3,5,8,10,12-hexaazacyclotetradecane nickel(II) cation and 5,11,17,23-tetrakis(*tert*-butyl)-25,26,27,28-tetrakis(carboxymethoxy)calix[4]arene.



**Fig. 2** ORTEP drawings of the asymmetric unit of complex **1** (a) and a part of the polymeric chain in **2** (b) with a partial numbering scheme (ellipsoids at the 30% probability level; non-relevant hydrogen atoms in **1** and **2** as well as the disordered *tert*-butyl group and solvent molecules in **2** are omitted for clarity; hydrogen bonds are shown as dotted lines; for the values of selected interatomic distances and angles see Table S2, ESI†).

85.7(1)°) and their increase in the 6-membered ones (average values: 92.9(1)° and 94.2(1)°, respectively).

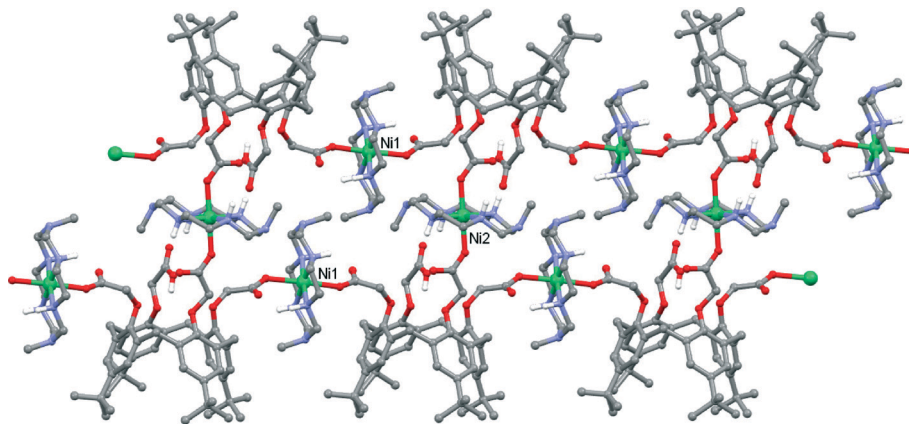
The phenoxyacetic acid fragments of  $\text{HCCA}^{3-}$  (designated further according to the notation of the corresponding ether oxygen atoms) can be divided into two types depending on their orientation relative to the conventional central axis of calix[4]arene. Those coordinated to Ni1 ( $\{O1\}$  and  $\{O5\}$ ) have lateral orientation (dihedral angles  $C_{\text{aromatic}}-O-C_{\text{methylene}}-C_{\text{carboxyl}}$ : 85.2° and 81.0°, respectively), while the others are tentatively coaxial (130.1° for  $\{O2\}$  coordinated to Ni2 and 170.0° for neutral  $\{O8\}$ ). The calix[4]arene platform as a whole adopts a *cone* conformation which is characterized by different inclinations of the planes of the benzene ring relative to the mean  $C_4$  plane of the bridging methylene groups (49.2, 59.1, 68.4 and 71.9° for  $\{O8\}$ ,  $\{O2\}$ ,  $\{O5\}$  and  $\{O1\}$ , respectively). Obviously, smaller values for the first three ones are explained by the formation of trifurcating hydrogen bonds between the neutral carboxylic group and ether oxygen atoms of the neighbouring substituents (Table S3, ESI†). Thus, the neutral carboxylic substituent

shrinks the lower rim of the ligand by hydrogen bonds and from this point of view it resembles endocoordinated alkaline metal ions in the complexes of calix[4]arene carboxylates.<sup>8–13</sup>

The carboxylic calix[4]arene in **2** acts as a tris(monodentate) bridging ligand. This mode of coordination results in the formation of a ladder-type 1D polymeric chain running down the crystallographic *b* axis (Fig. 3).

The lengths of this ladder are formed by Ni1 macrocyclic cations bridged *via* interaction with  $\{O1\}$  and  $\{O5\}$  lateral carboxylic groups of calix[4]arenes while the steps represent centrosymmetric macrocyclic cations Ni2 coordinated to  $\{O2\}$  carboxylic groups (the distances Ni1⋯Ni1 and Ni2⋯Ni2 along the *b* axis are both 15.324 Å). The mean NiN<sub>4</sub> planes of different metal ions are nearly perpendicular (80.8°) with the shortest Ni1⋯Ni2 distances equal to 8.260 and 9.786 Å.

Because of the presence of the voluminous calix[4]arene fragments the cross-section of the 1D chain has a dumbbell-like form and the chains are packed in a crystal parallel to each other with overlapping hydrophobic areas formed by *tert*-butyl substituents both in *a* and *c* directions (Fig. 4a).



**Fig. 3** Ball-and-stick representation (viewed down the crystallographic *a* axis) of the ladder-type 1D polymeric chain in **2** (non-relevant hydrogen atoms, disordered *tert*-butyl group and solvent molecules are omitted for clarity).

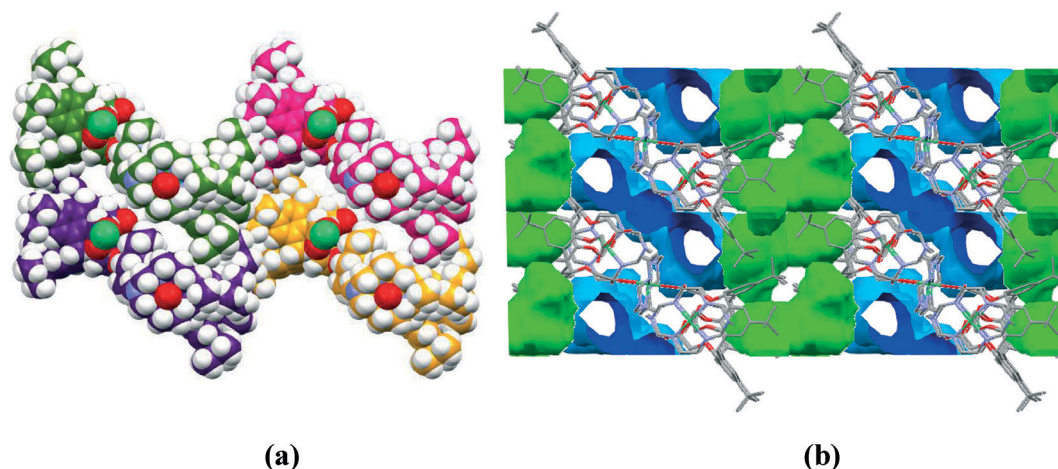


Fig. 4 (a) Space filling representation of the packing of 1D chains in **2** (solvent molecules are omitted; carbon atoms of different chains are shown in different colours) and (b) visualisation of non-polar voids (green) and polar channels (blue) (viewed down the crystallographic *b* axis).

Such a packing creates the ladder-like 1D channels running parallel to the *b* axis with a minimal opening of *ca.* 5 Å (estimated from the van der Waals surfaces) (Fig. 4b). These channels are filled with seven DMF molecules and one water molecule which form hydrogen bonds with amino groups of the macrocyclic cations and carboxylic groups of calix[4]arene (Table S3, ESI†). The volume of these polar (“hydrophilic”) channels calculated using PLATON<sup>20</sup> is 930 Å<sup>3</sup> (21% per unit cell volume). The remaining two DMF molecules occupy hydrophobic voids of the crystal (520 Å<sup>3</sup>, 12% per unit cell volume) (Fig. 4b). One of them resides in the cavity of the calix[4]arene and interacts with aromatic rings *via* three C–H⋯π contacts (H⋯C<sub>6</sub> centroid distances: 2.49, 2.61 and 2.64 Å) while the other is situated in the intermolecular hydrophobic region formed by *tert*-butyl groups with no recognizable intermolecular interaction with the environment. Thus, the total solvent accessible area in **2** calculated using PLATON<sup>20</sup> is 1450 Å<sup>3</sup> (33% per unit cell volume).

Photoluminescence properties of calixarenes are increasingly used for the development of analytical sensors. For these applications (usually in solution) the upper- or lower-rim modification of the calixarene platform with fluorogenic unit(s) is exploited.<sup>21</sup> At the same time, the luminescence properties of calixarene derivatives without fluorophore in the solid state are explored to a much lesser extent.<sup>12</sup> In order to study the light-emitting characteristics of such species the photoluminescence spectra of H<sub>4</sub>CCA and **2** were compared. Preliminary measurements show that at room temperature both solid H<sub>4</sub>CCA and **2** exhibit similar fluorescent emissions at λ<sub>max</sub> = 315 nm upon excitation at 275 nm (Fig. S5, ESI†) which can be assigned to intraligand π → π\* transitions in the aromatic part of the calixarene.<sup>12</sup> Taking into account that the presence of guest molecules can affect the luminescence behavior of PCPs (see, for example, ref. 22), this feature suggests the possibility of distinguishing guest molecules localized in different regions of **2** by fluorescence measurements. However, as one can see, the luminescence of H<sub>4</sub>CCA is essentially quenched by its coordination to the high-spin d<sup>8</sup> nickel(II) ion; therefore the

complexes of the non-transition metal ions with H<sub>4</sub>CCA seem to be more attractive. As promising substitutes for the cation in **2** we consider the macrocyclic zinc(II) complexes which are inclined to be isomorphous to the nickel(II) CPs<sup>23</sup> and this work is currently underway in our laboratory.

In conclusion, using the anionic form of the calix[4]arene tetracarboxylic acid and a macrocyclic nickel-containing cation, a ladder-type 1D coordination network has been obtained for the first time and structurally characterised in the crystalline phase. The porosity of the network is characterized by the presence of polar channels and non-polar voids formed by carboxylate substituents and azamacrocyclic cations on the one hand, and aromatic and *tert*-butyl substituents of the calix[4]arene on the other. The effect of the degree of ligand deprotonation and the structure of the connecting cation on the types of coordination networks as well as on the adsorption and photoluminescence properties of coordination polymers of this type are currently under study.

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## Notes and references

† Crystallographic measurements were made at 100(2) K using an «Xcalibur-3» diffractometer (Mo-Kα, λ = 0.71073 Å). Crystal data for [NiL](ClO<sub>4</sub>)<sub>2</sub> (1): C<sub>10</sub>H<sub>26</sub>Cl<sub>2</sub>N<sub>6</sub>NiO<sub>8</sub>, *M* = 487.98, monoclinic, space group *P*2<sub>1</sub>/*c*, *a* = 16.3018(5), *b* = 8.6598(2), *c* = 13.5660(4) Å, α = γ = 90, β = 112.177(4)°, *V* = 1773.44(9) Å<sup>3</sup>, *Z* = 4, *D*<sub>calc</sub> = 1.828 g cm<sup>-3</sup>, *F*(000) = 1016, μ(MoKα) = 1.451 mm<sup>-1</sup>, 2θ<sub>max</sub> = 55°, 11 917 reflections measured, of which 3872 are unique (*R*<sub>int</sub> = 0.024), *R*<sub>1</sub> [*I* > 4σ(*I*)] = 0.036, *wR*<sub>2</sub> (all data) = 0.096. ‡ Crystallographic measurements were made at 100(2) K using a «Xcalibur-3» diffractometer (Mo-Kα, λ = 0.71073 Å). Crystal data for {[NiL]<sub>3</sub>(HCCA)<sub>2</sub>·9DMF·H<sub>2</sub>O}<sub>*n*</sub> (2): C<sub>161</sub>H<sub>265</sub>N<sub>27</sub>Ni<sub>3</sub>O<sub>34</sub>, *M* = 3299.13, triclinic, space group *P*1̄, *a* = 12.9588(4), *b* = 15.3239(5), *c* = 24.3358(9) Å, α = 78.225(3)°, β = 84.909(3)°, γ = 70.031(3)°, *V* = 4445.5(3) Å<sup>3</sup>, *Z* = 1, *D*<sub>calc</sub> = 1.232 g cm<sup>-3</sup>,

1  $F(000) = 1776$ ,  $\mu(\text{MoK}\alpha) = 0.391 \text{ mm}^{-1}$ ,  $2\theta_{\text{max}} = 50^\circ$ , 43 396 reflections measured, of  
which 15 046 are unique ( $R_{\text{int}} = 0.033$ ),  $R_1 [I > 4\sigma(I)] = 0.077$ ,  $wR_2$  (all data) = 0.234.

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