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Half-opened clamshell and one-dimensional chain structures constructed of bis(macrocyclic) dinickel(II) complexes with iodide and terephthalate anions

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Abstract

Two new dinickel(II) complexes with iodide and bridging terephthalate (tp^{2-}) dianionic co-ligands, namely $[Ni_2L]I_4 \cdot 3H_2O$ (**1**) and *catena*-poly[[{$Ni_2L(OH_2)_2$}$_2$ (μ-*endo*-tp)](μ-*exo*-tp)]$(ClO_4)_4 \cdot 4H_2O$ (**2**), where L represents the bis(macrocyclic) ligand 7,7′-(propane-1,3-diyl)bis{3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene}, have been synthesized and their structures determined by the single crystal X-ray analysis. In the form of an iodide salt, (**1**) adopts a half-opened clamshell. The crystal of (**2**) consists of one-dimensional cationic chains in which the tetranuclear units, [{$Ni_2L(OH_2)_2$}$_2$(μ-*endo*-tp)], are linked by *exo*-bridging terephthalate anions.

Keywords: Synthesis; Dinickel(II) complex; Bis(macrocycle); One-dimensional chain; Half-opened clamshell; Terephthalate

A number of bis(macrocyclic) metal complexes, in which two macrocycles are linked by various functional groups, have been synthesized, and their structures and properties, which are different to those observed for the corresponding monomacrocyclic complexes, have gradually been elucidated [1–3]. For bis(macrocyclic) dimetal complexes, in which two identical macrocycles are linked with a polymethylene ($–(CH_2)_n–$, $n = 2, 3, 4$) bridge, several forms are possible because of the structural flexibility of the bridge (Scheme 1). Among these, the closed and half-opened clamshell forms are especially interesting, because the pseudo face-to-face structures offer the possibility of studying the cooperative effects of two metal centers and/or two macrocycles, such as the inclusion of small molecules between the two macrocycles. We previously reported a half-opened clamshell structure for the dicopper(II) complex and a closed form for the dinickel(II) complex containing a 2-hydroxytrimethylene-bridged bis(macrocyclic) ligand, in which the bridge contains a coordinating hydroxyl group [3].

In the present paper, we report the synthesis of two new dinickel(II) complexes with iodide and bridging terephthalate (tp^{2-}) dianionic co-ligands, namely $[Ni_2L]I_4 \cdot 3H_2O$ (**1**) and *catena*-poly[[{$Ni_2L(OH_2)_2$}$_2$(μ-*endo*-tp)](μ-*exo*-tp)]-$(ClO_4)_4 \cdot 4H_2O$ (**2**), where L represents a bis(macrocyclic) ligand which does not contain coordinating groups in the trimethylene bridge, 7,7′-(propane-1,3-diyl)bis{3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene}, and the elucidation of their structures by single crystal X-ray analysis. A half-opened clamshell form and a one-dimensional cationic chain structure were found for (**1**) and (**2**) respectively. Although many terephthalate-linked monomacrocyclic metal complexes have been reported [4], the chain structure found in this study is a rare example of a dimetal complex with bis(macrocycles) tethered by a polymethylene bridge.

The iodide salt of the dinickel(II) complex, $[Ni_2L]I_4 \cdot 3H_2O$ (**1**) [5], was prepared by addition of an excess amount of sodium iodide to an aqueous solution

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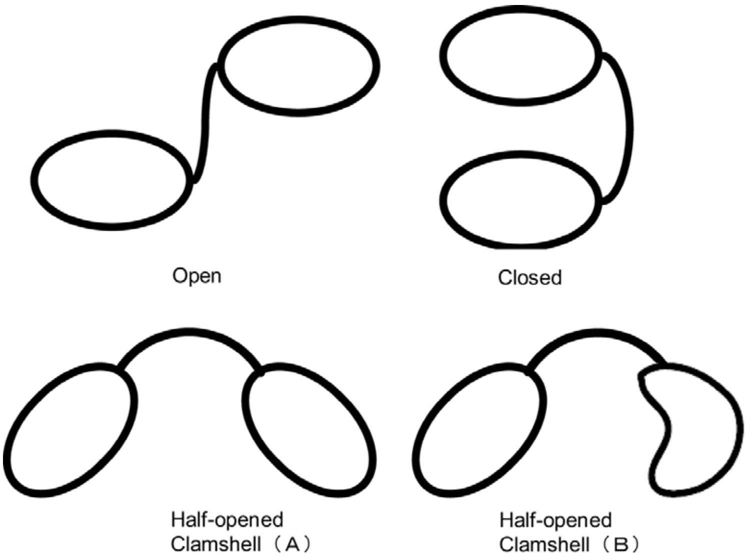

Scheme 1. Possible forms of bis(macrocycles) linked by a polymethylene bridge.

of $[Ni_2L](ClO_4)_4 \cdot H_2O$ (**3**), which was synthesized by the previously reported method [6]. Recrystallization of the iodide from water yielded dark violet crystals suitable for X-ray structural analysis. The diffuse-reflectance spectrum of a powder sample of (**1**) (intense, broad absorption bands around 360 and 550 nm) did not correspond to those of four-coordinate square-planar nickel(II) complexes such as the starting complex (**3**) (orange, λ_{max}: 468 nm), nor to those of six-coordinate nickel(II) complexes, but was very similar to those of five-coordinate species of analogous macrocyclic nickel(II) complexes [7].

The bis(macrocyclic) dinickel(II) complex (**1**) adopts a half-opened clamshell form (A), as shown in Fig. 1. The trimethylene bridge spreads out in a zigzag form and the two macrocyclic rings adopt a *syn*-geometry with respect to the trimethylene bridge (Ni(1)–Ni(2): 7.830(3) Å). Each of the tetraaza macrocycles coordinates to a nickel(II) ion in square planar fashion. The angle between the two macrocyclic mean-planes comprised of N(3), N(7), N(11), N(17) and N(21), N(25), N(29), N(35), respectively, was found to be 87°. The cavity in this half-opened clamshell dinickel (II) complex hosts two water molecules (O(38), O(39)) and one non-coordinating iodide anion (I(2)). The iodide ions I(1) and I(4) can be assumed to be loosely bound to the nickel centers to form a pseudo-square-pyramidal geometry, which is in accord with the above-mentioned diffuse-reflectance spectrum of (**1**). The Ni–I distances are very long, at I(1)–Ni(1): 3.294(2) and I(4)–Ni(4): 3.453(2) Å.

The reaction of (**3**) with one equivalent of sodium terephthalate in aqueous solution afforded crystals of a complex with a one-dimensional cationic chain, *catena*-poly[[{$Ni_2L(OH_2)_2$}$_2$(μ-*endo*-tp)](μ-*exo*-tp)]$(ClO_4)_4 \cdot 4H_2O$

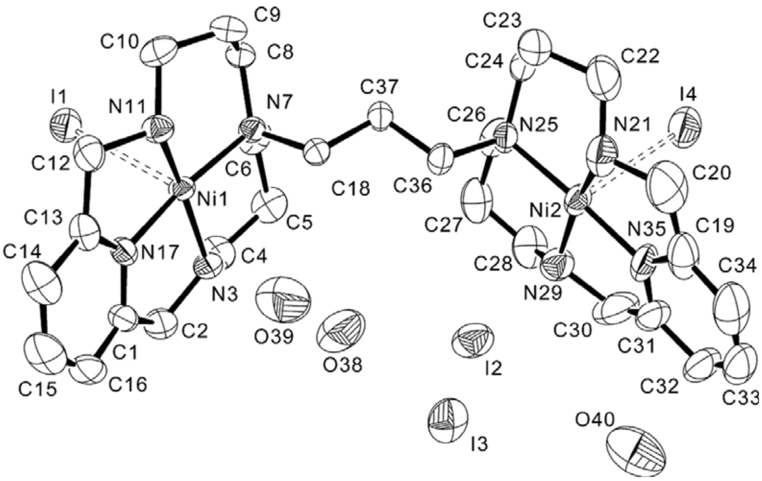

Fig. 1. The structure of $[Ni_2L]I_4 \cdot 3H_2O$ (**1**). Selected bond lengths (Å) and bond angles (°): Ni(1)–N(17) 1.844(7), Ni(1)–N(11) 1.947(7), Ni(1)–N(3) 1.957(7), Ni(1)–N(7) 1.971(7), Ni(2)–N(35) 1.845(8), Ni(2)–N(21) 1.943(10), Ni(2)–N(29) 1.960(10), Ni(2)–N(25) 1.968(7), N(17)–Ni(1)–N(11) 83.4(3), N(17)–Ni(1)–N(3) 83.6(3), N(11)–Ni(1)–N(7) 96.2(3), N(3)–Ni(1)–N(7) 94.7(3), N(35)–Ni(2)–N(21) 84.9(4), N(35)–Ni(2)–N(29) 82.6(4), N(21)–Ni(2)–N(25) 95.1(4), N(29)–Ni(2)–N(25) 96.7(4).