



## Synthesis and crystal structure of a new polymer built from a cyano nickel(II) oxa-azamacrocyclic complex

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### Abstract

The nickel(II) polymeric complex  $\{[\text{Ni}_6(\text{[22-HMTADO]}_3(\text{CN})_4)[\text{Ni}(\text{CN})_4] \cdot 5\text{H}_2\text{O} \cdot 8\text{CH}_3\text{OH}\}_n$  (III), where  $\text{H}_2\text{[22-HMTADO]} = 5,5,11,17,17,23\text{-hexamethyl-3,7,15,19-tetraazatricyclo[19,3,1,1}^{9,13}\text{]hexacos-1(25),2,7,9,11,13(26),14,19,21,23-decane-25, 26-diol}$ , is obtained from methanolic solution of  $[\text{Ni}_2(\text{[22-HMTADO]}(\text{CN})_2) \cdot 0.5\text{H}_2\text{O}$  (II) by slow evaporation method and characterized by X-ray crystal structure determination. The nickel(II) centers in the oxa-azamacrocyclic complex are bridged by the two phenolate oxygens as well as by  $\text{CN}^-$  and coordinated to carbon and nitrogen atoms derived from the bridging cyano ligand, forming square pyramidal and octahedral geometries, respectively. The mean nonbonded Ni–Ni intermetallic separation in the polymeric complex is 3.159 Å.

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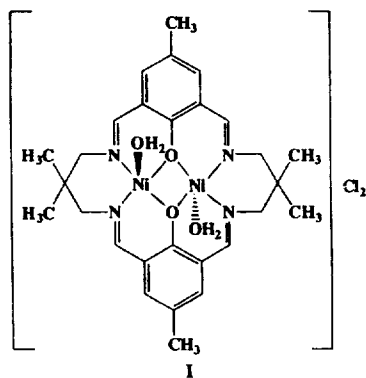
**Keywords:** Oxa-azamacrocyclic complex; Dinuclear nickel(II) complex; Bridging cyano ligand

Coordination polymers combined of polynuclear cyano complexes have been investigated for the chemical design of a new generation of magnetics, optics, electrical conductivity, catalysis and biology, all of which are derived from the effectiveness of the C- or N-bonded cyanide ion as a bridging ligand between two metal ions [1–6]. Furthermore, homodinuclear oxa-azamacrocyclic complexes which possess donor atoms or groups, e.g., phenoxy oxygen atoms and imine nitrogen atoms, play a key role in the modeling of metallobiosites and in the search for appropriate systems for activating simple molecules owing to their special coordination ability with the transition metal ions [7–9].

A synthetic route for designing a heme-cyanide-copper bridged assembly of formula  $[(\text{OEP-CH}_2\text{CN})\text{Fe-}$

$\text{NC-Cu}(\text{Npy}_3)]\text{ClO}_4$  (where OEP = the dianion of 2,3,7,8,12,13,17,18-octaethylporphyrin), containing the high-spin bridge Fe(II)–NC–Cu(I) in end-to-end fashion, has been proposed [10]. Using  $[\text{M}(\text{CN})_4]^{2-}$  (M = Ni, Pd or Pt),  $[\text{Fe}(\text{phen})_2(\text{CN})_2]$  and  $[\text{M}(\text{CN})_6]^{3-}$  (M = Fe, Cr or Co) as the precursor of the cyano moiety, a few cyanide-bridged lanthanide-transition metal complexes having variable molecular structures including dinuclear or oligonuclear discrete units have been reported [11–13]. The present crystal structure of the title coordination polymer  $\{[\text{Ni}_6(\text{[22-HMTADO]}_3(\text{CN})_4)[\text{Ni}(\text{CN})_4]\}_n$  ( $\text{H}_2\text{[22-HMTADO]} = \text{L}_m = 5,5,11,17,17,23\text{-hexamethyl-3,7,15,19-tetraazatricyclo[19,3,1,1}^{9,13}\text{]hexacos-1(25),2,7,9,11,13(26),14,19, 21,23-decane-25,26-diol}$ ) is the first report where in the homodinuclear oxa-azamacrocyclic complex, central nickel(II) ions are bridged by the two phenolate oxygens as well as by cyanides in end-to-end type. We report here two new nickel(II) oxa-azamacrocyclic complexes.

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Reaction of nickel chloride hexahydrate and a mixture of 2,6-diformyl-*p*-cresol with 2,2-dimethyl-1,3-propanediamine in methanol provided the pale green materials analyzing as  $[\text{Ni}_2(\text{[22]-HMTADO})(\text{OH}_2)_2]\text{Cl}_2 \cdot \text{H}_2\text{O}$  (I) [ref. Crystallographic data of  $[\text{Ni}_2(\text{[22]-HMTADO})(\text{OH}_2)_4]\text{Br}_2 \cdot 10\text{H}_2\text{O}$ : Deposition No. CCDC-271155]. A dark green species  $[\text{Ni}_2(\text{[22]-HMTADO})(\text{CN})_2] \cdot 0.5\text{H}_2\text{O}$  (II) was prepared by reacting complex I with an aqueous solution of NaCN. The green polymeric single crystal of  $\{[\text{Ni}_6(\text{[22]-HMTADO})_3(\text{CN})_4][\text{Ni}(\text{CN})_4] \cdot 5\text{H}_2\text{O} \cdot 8\text{CH}_3\text{OH}\}_n$  (III) suitable for X-ray diffraction study was grown from methanolic solution of II over 2 mon at room temperature.

The molar conductivity measurement of complexes I and II exhibits 205 (water) and  $9.5 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$  (methanol), respectively. The formation of binuclear Ni(II) complex, inferable from elemental analysis and molar conductance of the I and II, is evidenced by characteristic IR absorption bands and mass spectrum. For complex I, strong evidence that aldehyde groups had been completely converted into Schiff base residues was provided by the disappearance of the aldehydic  $\text{C}=\text{O}$  stretching band at  $1680 \text{cm}^{-1}$  and the appearance of a strong band at  $1635 \pm 5 \text{cm}^{-1}$  assigned to  $\nu(\text{C}=\text{N})$  stretching band [14]. Wide bands resulting from O–H stretching vibration of the coordinated and hydration water molecules emerge at  $3196$  and  $3313 \text{cm}^{-1}$ , respectively [15,16]. Complex II displays a peak for CN stretching at  $2127 \text{cm}^{-1}$ . The FAB mass spectrum of I has four dominant ion peaks

centered around  $m/z$  648.8, 610.7, 575.6 and 518.5, which are ascribed to the  $[\text{Ni}_2(\text{[22]-HMTADO})\text{Cl}_2]^+$ ,  $[\text{Ni}_2(\text{[22]-HMTADO})\text{Cl}]^+$ ,  $[\text{Ni}_2(\text{[22]-HMTADO})]^+$  and  $[\text{Ni}(\text{[22]-HMTADO})]^+$ , respectively, confirming the stability of the macrocycle in the metal complex [17]. Complex II give peaks due to  $[\text{Ni}_2(\text{[22]-HMTADO})(\text{CN})]^+$ ,  $[\text{Ni}_2(\text{[22]-HMTADO})]^+$  and  $[\text{Ni}(\text{[22]-HMTADO})]^+$ , at  $m/z$  599.3, 575.2 and 518.2. These major peaks are associated with peaks of mass one or two greater or less, which are attributed to protonated/deprotonated forms. This also accounts for the slight ambiguities in making assignments.

Compound III consists of a packing of polymeric  $[\text{Ni}_6(\text{[22]-HMTADO})_3(\text{CN})_4]^{2+}$  cations and  $[\text{Ni}(\text{CN})_4]^{2-}$  anions with five water and eight methanol molecules (Fig. 1). The structure of the chain by cationic dinuclear complex  $[\text{Ni}_6(\text{[22]-HMTADO})_3(\text{CN})_4]^{2+}$  shows that the two nickel(II) centers are bridged by the two phenolate oxygens as well as by  $\text{CN}^-$  as shown in Fig. 2. The central nickel ions are coordinated to carbon and nitrogen atoms derived from the bridging ligand, forming square pyramidal and octahedral geometries, respectively and has  $\text{N}_2\text{O}_2$  equatorial donors provided by the oxa-azamacrocyclic

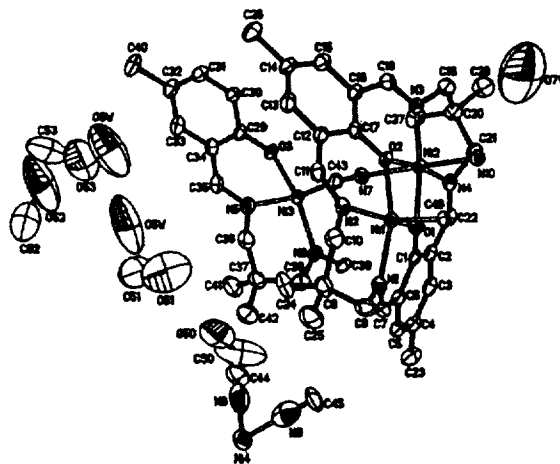


Fig. 1. Structural diagram of  $\{[\text{Ni}_6(\text{[22]-HMTADO})_3(\text{CN})_4][\text{Ni}(\text{CN})_4] \cdot 5\text{H}_2\text{O} \cdot 8\text{CH}_3\text{OH}\}_n$  with the asymmetric atom-labeling scheme.

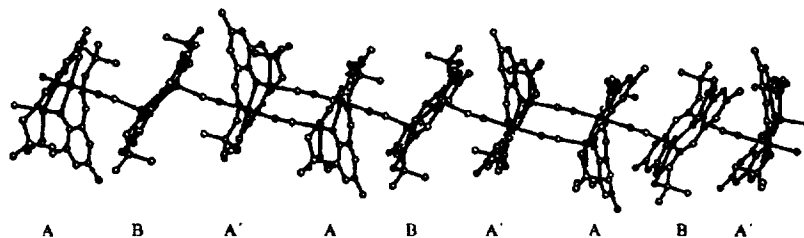


Fig. 2. Perspective view of the chain of  $[\text{Ni}_6(\text{[22]-HMTADO})_3(\text{CN})_4]^{2+}$  cation; (A): Ni(1) and Ni(2) forms square pyramidal and octahedral geometry, respectively, and methyl groups {C(24) and C(26)} attached to each lateral chain C(1) and C(12) are situated *cis* form. (B): Ni(3) and Ni(3)<sup>#1</sup> form *trans*-square pyramidal geometry, and methyl groups {C(41) and C(41)<sup>#1</sup>} are situated *trans* form. (A'): this species is an identical counterpart of (A).

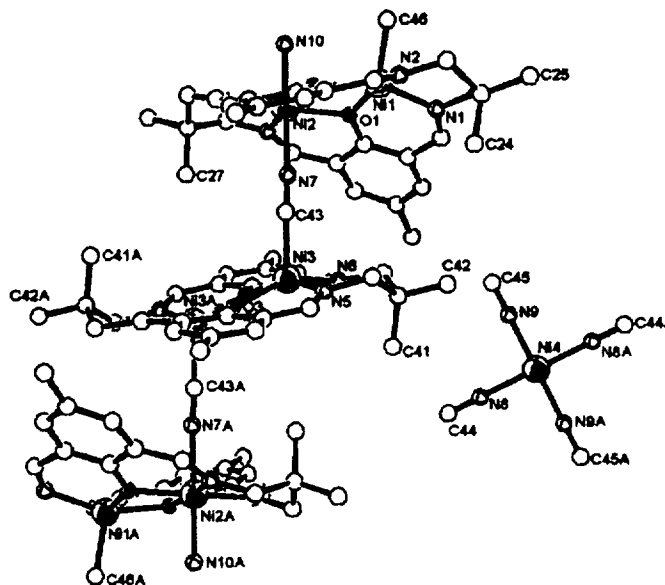


Fig. 3. The view of the CN-bridged polymeric  $\{[Ni_6(22\text{-HMTADO})_3(CN)_4][Ni(CN)_4]\}_n$  without  $H_2O$  and  $CH_3OH$ .

ligand. In the tetracyanonickelate moiety, the nickel ion is four coordinated by four cyanide–nitrogen atoms in a square-planar arrangement and the mean bond lengths of Ni–N (1.919 Å) and N–C (1.131 Å) (Fig. 3).

The polar guest  $[Ni(CN)_4]^{2-}$ , methanol and water are accommodated among  $[Ni_6(22\text{-HMTADO})_3(CN)_4]^{2+}$  chains. In the crystal packing of complex II the water molecule is involved in two intermolecular hydrogen bonds: O–H...O type hydrogen bonds with one of the hydrogen atoms of each water molecule {Ow(1)–Ow(3); 3.731 Å} and with O–H of a methanol solvent {O(50) (1 + x, y, z)–Ow(3); 2.889 Å}.

The Ni–N bond lengths is shorter than Ni–O bond lengths, indicating nitrogen atoms in the macrocycle have stronger affinity to Ni(II) ions, and this is responsible for its highest stability to Ni(II) ions. The Ni–μ(C or N)–CN bond lengths {Ni(3)–C(43) = 2.004(5) Å, Ni(2)–N(7) = 2.147(4) Å} are in accordance with the reported values for  $[Ni(TIM)][Ni(CN)_4]$  (TIM = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene) [18], but are longer than those in other nickel complex {Ni–C = 1.868(7) Å, Ni–N = 2.102(5) Å} [19]. The longer Ni–μ(C or N)–CN bond lengths in the title compound are due to the stronger Ni–N<sub>macrocycle</sub> interaction. The bridging cyano ligand linking adjacent macrocyclic components deviate significantly from the ideal value of 180° {C–N–Ni = 168.5(4)° and N–C–Ni = 171.6(5)°} due to the geometrical constraints associated with the oxa-azamacrocyclic. The two nickel(II) ions are separated by Ni(1)···Ni(2) (3.097 Å) and Ni(3)···Ni(3)<sup>#1</sup> (#1: –x + 1, –y + 1, –z + 1, 3.220 Å), with bridge angles of Ni(1)–O(1)–Ni(2) 99.36°, Ni(1)–O(2)–Ni(2) 99.48° and Ni(3)–

O(3)–Ni(3) 104.73°. These values is comparable with those observed in other oxa-azamacrocyclic complexes [20–22]. And the bond angles of N(1)–Ni(1)–N(2), O(1)–Ni(2)–O(2), N(5)–Ni(3)–N(6) and O(3)–Ni(3)–O(3) are 94.13, 79.85, 95.10 and 75.27°, respectively.

#### Supplementary information

Crystallographic data for the structural analyses have been deposited with Cambridge Crystallographic Data Center (Deposition No. CCDC-283045). The 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 CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; E-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

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