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Tuning the topologies of Co(II) and Ni(II) complexes with EDTA, 1,3-PDTA and 1,4-BDTA ligands: Synthesis and spectroscopic data of $[Mg(H_2O)_6][Co(1,4\text{-bdta})] \cdot 3H_2O$ and $[Mg(H_2O)_6][Ni(1,4\text{-bdta})] \cdot 3H_2O$ complexes, and the X-ray structure of their chiral crystals

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Abstract

The hexadentate complexes $[Mg(H_2O)_6][Co(1,4\text{-bdta})] \cdot 3H_2O$ (**a**) and $[Mg(H_2O)_6][Ni(1,4\text{-bdta})] \cdot 3H_2O$ (**b**) (where 1,4-bdta represents the 1,4-butanediaminetetraacetate ion) have been synthesized and characterized by electronic absorption spectroscopy and X-ray crystallography. The complexes (**a**) and (**b**) form isomorphic crystals that undergo a spontaneous resolution during the crystallization process yielding either enantiopure Λ (space group $P6_1$) or Δ (space group $P6_5$) isomers. The $[M(1,4\text{-bdta})]^{2-}$ (M = Co(II) (**a**) and Ni(II) (**b**)) and $[Mg(H_2O)_6]^{2+}$ octahedra are arranged in hydrogen bonded 2D-layers. Interception of these layers results in chiral channels filled with water molecules, which together with uncoordinated carboxylate oxygens of the complex anion, form mono-spiro chain that propagates in a helical manner along the *c*-direction. To the best of our knowledge, this is the first report on spontaneous resolution involving 1,4-bdta ligand and one of a few reports that concern conglomerate crystallization of $M(II)(N_2O_4)$ complexes. The electronic absorption spectra of $[Co(1,4\text{-bdta})]^{2-}$ and $[Ni(1,4\text{-bdta})]^{2-}$ are presented and discussed in comparison with those of similar complexes and with reference to the varying topologies of these complexes.

Keywords: EDTA-type chelates of Co(II) and Ni(II); Syntheses and X-ray crystal structures; Conglomerate crystallization; Spontaneous resolution; Chiral channel structures; Hydrogen bonding

1. Introduction

In a process of a systematic study of metal(II) complexes containing aminopolycarboxylate edta-type ligands we have focused our attention on the influence of the diamine ring size (five-, six- and seven-membered) on the coordination number and geometry, and complex stability. As we widely use in our studies X-ray crystallography, and the investigated ligands form a dissymmetric ensemble upon coordination to metal centers, we were also interested in the possibility of conglomerate crystallization of these metal(II) complexes as compared with their metal(III) analogues. The hexadentate ligand, the 1,3-propanedia-

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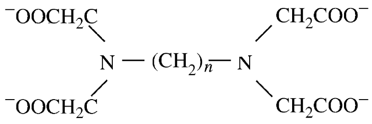
minetetraacetate ion (1,3-pdta), has been used for preparation of hexadentate complexes with many metal ions [1–9]. The structural characteristics of the hexadentate [M(1,3-pdta)]$^-$ (M(III) = Co [1], Cr [2], Rh [2], Fe [3] and V [4]), [M(1,3-pdta)]$^{2-}$ (M(II) = Cu [5], Ni [6], Co [7], Mg [8] and Zn [9]), [Ca(1,3-pdta)(H_2O)]$^{2-}$ [8] and [Cd(1,3-pdta)(H_2O)]$^{2-}$ [9] complexes have been determined by single-crystal X-ray crystallography. Four out of seventeen 1,3-pdta complexes: Na[Cr(1,3-pdta)] · $3H_2O$ [2], Na[V(1,3-pdta)] · $3H_2O$ [4], Na[Fe(1,3-pdta)] · $3H_2O$ [3b] and K[Co(1,3-pdta)] · $2H_2O$ [1] have been spontaneously resolved by crystallization. Crystals of the first three complexes have been found to be isomorphic (space group $P2_12_12_1$) with those of Na[Rh(1,3-pdta)] · $3H_2O$ [2] which were resolved based on different solubility of diastereomeric salt pairs using as a resolving agent $(-)_{589}$-[Co(en)$_2$-(ox)]Br · H_2O. In the case of K[Co(1,3-pdta)] · $2H_2O$ [1] the spontaneous resolution has lead to the enantiomerically enriched product which crystallizes in space group $C222_1$ (standard setting). However, the conglomerate crystallization[1] has not been evidenced thus far neither in the case of (1,3-propanediaminetetraacetato)metal(II) [5–9] nor 1,4-bdta [1,4-butanediaminetetraacetate ion] complexes [10,11].[2]. The metal(II) ions of the ionic radii of about 0.8–0.9 Å with 1,3-pdta ligand form octahedral complexes of the [M(H_2O)$_6$][M′(1,3-pdta)] · $2H_2O$ type (M(II), M′(II) = Mg,Cu [5a]; Mn,Cu [5b]; Mg,Ni [6]; Mg,Co [7]; Co,Co [7]; Mg,Mg [8]; Mg,Zn [9] and Zn,Zn [9]), which crystallize in the space group *Pnna*, forming the isomorphic series. The 1,3-pdta ligand with spherically symmetric metal ions of the ionic radii greater than 0.9 Å tends to form hexadentate complexes of CN higher than six, as evidenced by the crystal structures of the [Ca(H_2O)$_3$-Ca(1,3-pdta)(H_2O)] · $2H_2O$ [8] (CN = 8, space group $P\bar{1}$), and isomorphic hexaaquamagnesium(II) crystals of seven-coordinated [Cd(1,3-pdta)(H_2O)]$^{2-}$ [9] and [Mn(1,3-pdta)(H_2O)]$^{2-}$ [12] complexes which crystallize as dihydrates in *Pbcn* space group.

Due to the presence of the six-membered backbone diamine ring in the M-1,3-pdta system, the 1,3-pdta complexes are less strained with respect to the corresponding edta (edta = ethylenediaminetetraacetate ion) complexes [6]. The hexadentate ligand, 1,4-bdta, has lengthened diamine chain with respect to both ligands, edta and 1,3-pdta (Scheme 1), and is able to form a seven-membered backbone diamine ring upon coordination with metal ions. However, stabilization due to chelation, known as a chelate effect, is usually most pronounced for 5- and 6-membered rings. Larger rings offer a rapidly decreasing advantage for coordination to the second site [13]. This might be one of the reasons why crystallographic results concerned with the hexadentate complexes of 1,4-bdta are rather scarce, being limited to only [Co(1,4-bdta)]$^-$ [10], [Cr(1,4-bdta)]$^-$ [11] and [V(1,4-bdta)]$^-$ [11]. In this paper we report the syntheses of new hexadentate [Mg(H_2O)$_6$][Co(1,4-bdta)] · $3H_2O$ (**a**) and [Mg(H_2O)$_6$][Ni(1,4-bdta)] · $3H_2O$ (**b**) complexes, as well as the Ba_2(1,4-bdta) · $2H_2O$ complex which was used for the preparation of the complexes (**a**) and (**b**). For complexes (**a**) and (**b**) we provide electronic absorption spectroscopy characterization and the description of their crystal structures. From the solutions of [Mg(H_2O)$_6$][Co(1,4-bdta)] · $3H_2O$ (**a**) and [Mg(H_2O)$_6$]-[Ni(1,4-bdta)] · $3H_2O$ (**b**), conglomerate crystallization has been observed. The incidence of conglomerate crystallization, being a subject of intense study by Bernal and co-workers [14–20], is relatively rare: to the best of our knowledge the reported crystal structures represent the first case of spontaneous resolution involving 1,4-bdta ligand and one of a few reports dealing with conglomerate crystallization of transition metal(II) complexes with N_2O_4 type of ligands [21–25].



n = 2: edta; *n* = 3: 1,3-pdta; *n* = 4: 1,4-bdta

Scheme 1.

2. Experimental

2.1. Compounds preparation

All commercially obtained reagent-grade chemicals were used without further purification.

2.1.1. Preparation of barium 1,4-butanediaminetetraacetate dihydrate, Ba_2 (1,4-bdta) · $2H_2O$

Monochloroacetic acid (86.00 g, 0.91 mol) was dissolved in 100 cm^3 of H_2O and cooled in an ice bath. A cooled solution of NaOH (36.40 g, 0.91 mol) in 90 cm^3 H_2O was added drop by drop, and the rate of addition was adjusted so that the temperature remained below 15 °C. To this solution, 1,4-butanediamine (17.63 g, 0.20 mol) dissolved in 50 cm^3 of H_2O was added, and the solution was allowed to stir for 10 min at 15 °C. Then, the reaction mixture was refluxed (80–90 °C) for 4 h, and an additional amount of NaOH (36.00 g, 0.90 mol) in 60 cm^3 of H_2O was added drop by drop to keep the pH in the range 7–8. The volume of the resulting solution was reduced to 200 cm^3 and the deposited NaCl was filtered out. The filtrate was heated at 90 °C and pH was adjusted to *ca.* 9, then to this filtrate a hot solution of $BaCl_2$ · $2H_2O$ (98.0 g, 0.40 mol) in 200 cm^3 of H_2O was added. Stirring with maintenance of the temperature at 90 °C was continued for 2 h. The insoluble white precipitate of Ba_2(1,4-bdta) · $2H_2O$ was collected

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[1] Conglomerate crystallization is the phenomenon wherein a solution of racemate precipitates enantiomorphic crystals each of which contains exclusively a single enantiomer (homochiral crystals).

[2] The *P*1 chiral space group, assigned to K[Cr(1,4-bdta)] · H_2O crystals [11a] has been corrected by Herbstein and co-workers [11b] to centrosymmetric $P\bar{1}$.