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Coordination ability of *trans*-cyclohexane-1,2-diamine-*N*,*N*,*N*',*N*'-tetrakis(methylenephosphonic acid) towards lanthanide(III) ions.

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Streszczenie

The proton and metal complex equilibria of trans-cyclohexane-1,2-diamine-N,N,N',N'-tetrakis(methylenephosphonic acid) (CDTP) with lanthanide(iii) ions, where Ln(III) = La(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Ho(III) and Lu(III) were studied. The stoichiometry, protonation and complex formation constants were determined by potentiometric titration at 25.0 degrees C and ionic strength of 0.1 mol dm(-3) (KCl). All metal ions form several species: [LnH4L]-, [LnH3L](2-), [LnH2L](3-), [LnHL](4-), [LnL](5-), [LnH(-1)L](6-) and [LnH(-2)L](7-) in the pH range between 2 and 11. The stability constants log beta(LnL) were found to be between 14.7 and 16.7. The studied complexes were also characterized by spectroscopic methods (31P NMR, UV-Vis absorption and emission spectroscopy). These studies allowed to reveal a distinct structural change of the Ln(III)-CDTP complex which occurs between protonated and hydroxy species in solutions at pH around 7.5. The major change is caused by the involvement of both nitrogen donors in the metal ion coordination occurring in ML species. The data obtained from UV-Vis spectroscopy allowed to draw conclusions about complex symmetry and to estimate a number of coordinated water molecules. The hydration number or more precisely the number of two OH oscillators was found to be approximately one in all species formed over the pH range between 5 and 10. The structure of the major hydroxy complex was supported by X-ray crystallographic data. The crystal structures of the Eu(III) and Tb(III) complexes clearly show that the CDTP ligand is coordinated to the Ln(III) ion by two nitrogen and four oxygen atoms in such a way that only one oxygen atom from each phosphonic group is placed in the lanthanide inner sphere. The monomeric complex anion is connected to a symmetry related ion through short hydrogen bonds formed by two hydroxy ions and one water molecule. In this way the two neighbouring anions form a quasi-dimer in which one of the Ln(III) ion is seven-coordinate (two N atoms, four O atoms and one hydroxy ion) and the other is eight-coordinate (two N atoms, four O atoms, one hydroxy ion and one water molecule).

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