Unusual coordination behaviour of a phosphonate- and pyridine-containing ligand in a stable lanthanide complex.

Autorzy

Joanna Gałęzowska

Rafał Janicki

Henryk Kozłowski

Anna Mondry

Piotr Młynarz

Łukasz Szyrwiel

Rok wydania

2010

Czasopismo

European Journal of Inorganic Chemistry

Strony

1696-1702

DOI

10.1002/ejic.201000058

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

An experimental study of the coordination of lanthanide ions with {ethane-1,2-diylbis[imino(pyridin-2-ylmethanediyl)]}bis(phosphonic acid), a ligand containing phosphonate and pyridine arms attached to the well-known ethylenediamine scaffold, is reported. The X-ray crystal structure of an anionic, octacoordinate Eu^{III} complex of the formula $[C(NH_2)]_6[Eu_2(L)_2(CO_3)_2]\cdot 8H_2O$ has been obtained and found to contain cyclic dimeric complex anions in which the coordination environment of each Eu^{III} ion is composed of three oxygen atoms from phosphonate groups, two nitrogen atoms from imino groups and one nitrogen atom from a pyridine group, a combination that has seldom been observed for Ln^{III} complexes. In order to check the coordination behaviour of the ligand, an investigation of the complexes in solution has been performed, which revealed a different coordination mode. The protonation constants of the free ligand and the stability constants of their complexes with selected lanthanide ions (La^{III}, Sm^{III}, Eu^{III}, Gd^{III}, Tb^{III}, Ho^{III} and Lu^{III}) have been determined potentiometricaly at 25 °C and an ionic strength of 0.1 M (KCl). The results obtained show the formation of monomeric, protonated ($[LnH_2L]$, $[LnHL]$) and nonprotonated ($[LnL]$) species in the pH range studied (2–11). The determined stability constants ($\log\beta_{LnL}$) are relatively high, varying between 14.96 and 16.42. The Eu^{III}**L** system was also fully characterized by means of UV/Vis spectroscopy, which indicated that the coordination process starts above pH 3 and remains constant in the range pH 4–10. In contrast to the crystal structure, solution NMR and luminescence studies suggested that the pyridine moieties are not present in the Ln^{III} coordination sphere. These results suggest that this ligand–unsaturated metal ion coordination sphere may provide a potential binding site for other target molecules.

Słowa kluczowe

lanthanides, N, P ligands, Stability constants, Coordination modes

Adres publiczny

https://doi.org/10.1002/ejic.201000058

Strona internetowa wydawcy

onlinelibrary.wiley.com