



Studies on zinc(II) complexes with *N*-thioacylamidophosphates: X-ray crystal structure of the [Zn(RC(S)NP(O)(OiPr)₂)₂] (R = NH₂, *t*BuNH, *c*-C₆H₁₁NH)

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ARTICLE INFO

Article history:

Received 27 September 2007

Accepted 12 March 2008

Keywords:

Organoelement analogues of β-dicarbonyl ligands

(Thioacylamido)phosphates

Zn(II) chelates

Heteroligand complexes

1,10-Phenanthroline

2,2'-Bipyridine

ABSTRACT

The photoluminescent properties of 17 zinc(II) chelates [Zn(RC(S)NP(O)(OiPr)₂-O,S)₂] (R = Ph (**1a**), PhNH (**1b**), *p*-BrPh (**1c**), *p*-MeOC₆H₄NH (**1d**), *p*-BrC₆H₄NH (**1e**), NH₂ (**1f**), *i*PrNH (**1g**), *t*BuNH (**1h**), Et₂N (**1i**), *c*-C₅H₁₀N (**1j**), *c*-OC₄H₈N (**1k**), *c*-C₆H₁₁NH (**1l**), aminobenzo-15-crown-5 (**1m**)) and [Zn(B)(RC(S)NP(O)(OiPr)₂-O,S)₂] (R = Ph, B = 2,2'-bipyridine (**2a**); R = Ph, B = 1,10-phenanthroline (**2b**); R = PhNH, B = 2,2'-bipyridine (**2c**); R = PhNH, B = 1,10-phenanthroline (**2d**)), are reported. Colorless and air/moisture stable chelate complexes of divalent zinc show blue emission in the solid state when excited with UV light. Complexes **1f**, **1h**, **1l** were investigated by single crystal X-ray diffraction. The zinc(II) atom in complexes **1f**, **1h**, **1l** is in a distorted tetrahedral O₂S₂ environment formed by the C=S sulphur atoms and the P=O oxygen atoms of two deprotonated ligands.

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1. Introduction

Up to now, large numbers of coordination complexes of the Zn(II) cation have been prepared by taking certain factors into account, such as the functionality, flexibility, symmetry and nature of donor centers of organic ligands and the coordination ability of the metal ion [1]. Among these, the construction of complexes with changeable geometry and structure, to the best of our knowledge, has become a widely propagated and popular subject. Such complexes are important in advanced materials such as optical devices, especially with luminescence properties [2]. One of the effective strategies to vary luminescent activity is to change the geometry and structure. This requires the synthesis of complexes by addition of a heteroligand to homoligand luminescence active complexes. These compounds might find applications as receptors with optical detecting properties.

The late transition metal ion complexes of *N*-acylthioureas R₂NC(S)NHC(O)R' [3] and their phosphoryl analogues based on thioureas R₂NC(S)NHP(O)(OR')₂ and thioamides RC(S)NHP(O)(OR')₂ [4,5, and references therein] are of interest due to their mag-

netic and photophysical properties. The 1,5-*X,S*-coordination of these ligand anions is typical for chelate complexes (e.g. [4–6]).

However, recent investigations have shown that the coordination mode of these ligands containing the RNH group towards Ni(II), Pd(II), Pt(II) [7,8], Cu(II) [9] and Cd(II) [10] cations depends on the presence of strong intramolecular NH...O=P or NH...O=C bonds. The thiourea ligands of common formula RNHC(S)NHP(O)(OR')₂ (NPTU) [8,9] are able to bind Ni(II), Pd(II) and Cu(II) cations through the C=S sulfur and P–N nitrogen atoms. The thiourea *n*PrNHC(S)NHC(O)*n*Pr [7] forms similar 1,3-*N,S*-chelate with the Pt(II) cation through the C=S sulfur and NC(O) nitrogen atoms.

Interestingly, the *N*-(*o*-nitrophenyl)-*N'*-(methoxycarbonyl)thiourea (HQ) in complex of formula [Cd(2,2'-bpy)Q₂] is also bound in the 1,3-*N,S*-fashion via the C=S sulfur and NC(O) nitrogen atoms [10]. However, the sulfur atom of the thiourea HQ does not coordinate to the Zn(II) ion. A monodentate coordination through the deprotonated nitrogen atom of the C(S)NC(O) moiety occurs in the chelate [Zn(2,2'-bpy)Q₂].

In the literature there is no information on crystal structure of NPTU complexes with the Zn(II) cation. In this connection it was interesting to investigate the structure and properties of some complexes of phosphorylated thioureas and thioamides and compares these with heteroligand analogues with participation of 2,2'-bipyridine (bpy) and 1,10-phenanthroline (phen) as additional donor ligands.

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