



Novel bicyclic hexanuclear copper(I) aggregate: Structure and solid state ^{31}P CPMAS NMR spectra of $[(\text{Cu}_3\text{L}_3)_2]$ and $[\text{Cu}(\text{PPh}_3)_2\text{L}]$ complexes of *N*-(diisopropoxythiophosphinyl)-*N'*-phenylthiourea (HL)

Felix D. Sokolov^a, Maria G. Babashkina^a, Franck Fayon^{b,c}, Aydar I. Rakhmatullin^{b,c}, Damir A. Safin^{a,*}, Tania Pape^d, F. Ekkehardt Hahn^d

^a A. M. Butlerov Chemistry Institute, Kazan State University, Kremlevskaya St. 18, 420008 Kazan, Russian Federation

^b CEMHTI-CNRS, 1D Avenue de la Recherche Scientifique, 45071 Orléans Cedex2, France

^c Université d'Orléans, Faculté des Sciences, Avenue du Parc Floral, BP 6749, 45067 Orléans Cedex2, France

^d Institut für Anorganische und Analytische Chemie, Westfälische Wilhelms-Universität Münster, Corrensstrasse 36, D-48149 Münster, Germany

ARTICLE INFO

Article history:

Received 13 June 2008

Received in revised form 26 August 2008

Accepted 6 October 2008

Available online 14 October 2008

Keywords:

Copper(I) complexes

Crystal structures

MAS NMR spectroscopy

N-Thiophosphorylthiourea

Polynuclear complexes

ABSTRACT

A new complex of *N*-thiophosphorylthiourea $\text{PhNHC}(\text{S})\text{NHP}(\text{S})(\text{O}i\text{Pr})_2$ (**HL**) of formula $[(\text{Cu}_3\text{L}_3)_2]$ has been synthesized and characterized by single crystal X-ray diffraction, FT-IR, ^1H , ^{31}P NMR in solution and by ^{31}P CPMAS NMR spectroscopy in the solid state. A comparison of the structure and the spectral parameters of $[(\text{Cu}_3\text{L}_3)_2]$ with those of the mononuclear analogue $[\text{Cu}(\text{PPh}_3)_2\text{L}]$ was performed. In the solid state the aggregate $[(\text{Cu}_3\text{L}_3)_2]$ represents the first example of a spontaneous “side-by-side” association of two neutral cyclic $[\text{Cu}_3\text{L}_3]$ moieties using two Cu–S–Cu bridges formed by the sulfur atoms of the PS-groups. The values of the $^1J(^{31}\text{P}_{-63,65}\text{Cu})$ and $^2J(^{31}\text{P}_{-31}\text{P})$ coupling constants of the $[\text{Cu}(\text{PPh}_3)_2]^+$ moiety in the solid state spectra are reported.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Data available in the literature demonstrate, that complexes of coinage metal cations with 1,3- and 1,5-bidentate ligands derived from sulfur- or selenium-containing phosphines, exhibit a clear propensity to form oligo- and polynuclear assemblies with structural features which depend on the conditions employed for their preparation and the nature of the ligand [1–3]. The investigation of the structure of such compounds, as a rule, is impossible without the use of single crystal X-ray diffraction techniques. The situation is further complicated by the problems encountered when attempting to grow single crystals and the tendency for form oligomeric aggregates.

Therefore the development of spectroscopic methods has been the focus of recent interest as such techniques not only provide information on the structure of a given compound but can also shed light on the mechanism of its formation. The literature contains reports on the successful application of solid state nuclear magnetic resonance for this purpose. For example, the solid-state ^{31}P and ^{65}Cu NMR spectroscopy allowed to determine successfully selected structural parameters of some polynuclear copper(I)

complexes like $[\text{Cu}_4\{\text{S}_2\text{P}(\text{OR})_2\}_4]$, $[\text{Cu}_6\{\text{S}_2\text{P}(\text{OR})_2\}_6]$ and $[\text{Cu}_8\{\text{S}_2\text{P}(\text{OR})_2\}_6(\mu^8\text{-S})]$ ($\text{R} = \text{alkyl}$) [3,4].

This type of researches is important not only for the understanding of the fundamental laws of polynuclear coordination structure formation, but also open the ways for further use of the formed molecules. The complexes of phosphorus-, sulfur- or selenium-containing ligands with coinage metals cations are of great interest due to their photophysical properties [5,6], their application for creation of chalcogenide nanoparticles [1c], and as models for biological objects [7].

Contrary to the dithiophosphate ligands, there is a lack of information about the structures of polynuclear copper(I) complexes containing *N*-thiophosphorylated thioureas and thioamides, $\text{RC}(\text{S})\text{NHP}(\text{S})\text{R}'_2$ ($\text{R} = \text{R}'_2\text{N}$, alkyl, aryl). The molecular structures of three polynuclear Cu^{I} complexes namely the cyclic trimers $[\text{Cu}_3\{\text{Et}_2\text{NC}(\text{S})\text{NP}(\text{S})(\text{OPh})_2\}_3]$ [8], $[\text{Cu}_3\{\text{MfC}(\text{S})\text{NP}(\text{S})(\text{O}i\text{Pr})_2\}_3]$ ($\text{Mf} = \text{morpholyn-}N\text{-yl}$) [9] and of an ionic aggregate $[\text{Cu}_{10}\{\text{PhNHC}(\text{S})\text{NP}(\text{S})(\text{OEt})_2\}_9]\text{ClO}_4$ [10], have been reported.

In this study, we describe the synthesis and the structural characterization of the new *N*-thiophosphorylthiourea $\text{PhNHC}(\text{S})\text{NHP}(\text{S})(\text{O}i\text{Pr})_2$ (**HL**) and of its polynuclear Cu^{I} aggregate $[(\text{Cu}_3\text{L}_3)_2]$ (**1**) (Chart 1). To the best of our knowledge, compound **1** represents the first example for the spontaneous “side-by-side” association of the two neutral cyclic $[\text{Cu}_3\text{L}_3]$ moieties to give a hexameric unit.

* Corresponding author. Fax: +7 843 254 37 34.

E-mail address: damir.safin@ksu.ru (D.A. Safin).