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Synthesis, structural analysis, and thermal and spectroscopic studies of methylmalonate-containing zinc(II) complexes

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ABSTRACT

The synthesis, crystal structure, thermal analysis and spectroscopic studies of five zinc(II) complexes of formulae $[Zn(Memal)(H_2O)]_n$ (**1**) and $[Zn_2(L)(Memal)_2(H_2O)_2]_n$ (**2**-**5**) [H_2Memal = methylmalonic acid, and L = 4,4′-bipyridine (4,4′-bpy) (**2**), 1,2-bis(4-pyridyl)ethylene (bpe) (**3**), 1,2-bis(4-pyridyl)ethane (bpa) (**4**) and 4,4′-azobispyridine (azpy) (**5**)] are presented here. The crystal structure of **1** is a three-dimensional arrangement of zinc(II) cations interconnected by methylmalonate groups adopting the μ_3-κ^2O:$\kappa O'$:$\kappa O''$:$\kappa O'''$ *coordination mode to afford a rare (10,3)-d* **utp***-network. The structures of the compounds* **2**-**5** *are also three-dimensional and they consist of corrugated square layers of methylmalonate-bridged zinc(II) ions which are pillared by bis-monodentate 4,4′-bpy (***2***), bpe (***3***), bpa (***4***) and azpy (***5***) ligands. The Memal ligand in* **2**-**5** *adopts the* μ_3-κO:$\kappa O'$:$\kappa O''$:$\kappa O'''$ *coordination mode. Each zinc(II) ion in* **1**-**5** *is six-coordinated with five (***1***)/four (***2**-**5***) methylmalonate-oxygen atoms, a water molecule (***1**-**5***) and a nitrogen atom from a L ligand (***2**-**5***) building distorted octahedral environments. The rod-like L co-ligands in* **2**-**5** *appear as useful tools to control the interlayer metal-metal separation, which covers the range 8.4311(5) Å (***2***) – 9.644(3) Å (***5***). The influence of the co-ligand on the fluorescence properties of this series of compounds has been analyzed and discussed by steady-state and time resolved spectroscopy on all five compounds in the solid state.*

1. Introduction

Self-assembly of metal ions and multidentate organic ligands has attracted great attention because organic spacers can alter inorganic microstructures, providing a promising route for the design of novel materials [1].

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To date, numerous coordination polymers with multifunctional frameworks have been synthesized. These hybrid inorganic-organic coordination polymers are interesting materials because of their potential applications in ion-exchange, catalysis, molecule adsorption, electric conductivities, magnetic and optical properties [2]. The architecture of the hybrid inorganic-organic networks is dependent on the geometrical preferences of the metal ions as well as on the organic linkers and blocking ligands, which exhibit remarkable diversity in their molecular structures. It deserves to be noted that in spite of the great number of results obtained and subsequent knowledge acquired, the rational design of functional materials is still at its exploratory stage and the construction of extended solids still remains unpredictable, due to many subtle interactions of reaction parameters such as temperature, time, pH value, solvent, synthetic route and stoichiometry.

Up to now, a great number of inorganic-organic hybrid coordination polymers have been synthesized based on strong covalent bonds or weak supramolecular connections such as hydrogen bonds and/or $\pi\cdots\pi$ interactions [3]. It has been documented that the geometries of the organic ligands have a great effect on the structural frameworks of such coordination polymers; thus, much effort has been devoted to modifying the building blocks and to controlling the assembled motifs for required products through the selection of different organic ligands. Previous studies have shown that rigid bridging ligands containing multicarboxylate groups are versatile ligands to afford moderately robust networks of variable dimensionality and porosity [4–6]. Also many compounds containing aliphatic carboxylates [deprotonated $HOOC(CH_2)_nCOOH$ derivatives] have been prepared and characterized [7]. In fact, the conformational flexibility of this type of ligands is reflected on the diversity of their connecting modes that lead to novel frameworks.

On the other hand, a rational approach to build three-dimensional structures is based on layered structural systems that can be pillared by organic linkers whose length can be modulated, aiming at fixing the interlayer separation. This strategy has been proved to be effective in the assembly of both non-covalent and covalent pillared networks [8,13a]. Rigid rod-like spacer molecules like 4,4′-bipyridine (4,4′-bpy) or 1,2-bis(4-pyridyl)ethylene (bpe) allow for some degree of control to be exerted upon the steric constrains of the assembly process and they have been used as ligands for the construction of dimensionality controlled metal-organic coordination frameworks [9–13].

Having in mind our previous results with the malonate dianion as a bridging ligand [14], and the more recent studies of copper(II) complexes with aryl/alkyl substituted malonate ligands [phenylmalonate (dianion of the phenylmalonic acid, H_2Phmal) [15] and methylmalonate (dianion of the methylmalonic acid, H_2Memal)] [13a,16], we undertook a systematic study of the structural possibilities offered by the zinc(II)/Memal^{2-}/L system (L being a rod-like bis-monodentate extended spacer). It is known that zinc(II) coordination complexes exhibit a wide range of structures ranging from simple chains (1D) to more complex, porous three-dimensional (3D) networks [17]. Previous attempts on complex formation between substituted malonate and zinc(II) ions yielded either mononuclear complexes using blocking ligands [18] or polynuclear malonate-bridged compounds with several co-ligands [19]. In particular, only five zinc(II) complexes of malonate/substituted malonate without coligands have been reported: three of them are polynuclear compounds of formulae $[Zn(R\text{-}mal)(H_2O)_m]_n$ [R-mal = 3-hydroxycyclobutane-1,1-dicarboxylate ($m = 2$), 2,2-dimethylmalonate ($m = 1$) and malonate ($m = 2$)] and the other two are mononuclear species of formula $[Zn(Hmal)_2(H_2O)_2]$ (H_2mal = malonic acid) [20].

The geometrical constraints caused by the insertion of a methyl group on the methylene carbon atom could induce different conformations of the resulting methylmalonate as a ligand when compared to its parent malonate group. At this respect, previous studies concerning the compounds $[Cu(Memal)(H_2O)]_n$, $[Cu_2(pyz)(Memal)_2]_n$ and $[Cu_2(4,4'\text{-}bpy)(Memal)_2(H_2O)_2]_n$, (pyz = pyrazine) showed that it is possible to exert some control over these conformations using the appropriate co-ligands [13a]. This series of complexes is particularly interesting because the bis-monodentate rod-like spacer acts as a pillar of the corrugated layers of methylmalonate-bridged copper(II) ions providing, thus, a safe strategy to tune the separation between magnetic layers.

In the present work, we focus on the synthesis, structural characterization, thermal behaviour and luminescent properties of five methylmalonate-containing zinc(II) complexes of formula $[Zn(Memal)(H_2O)]_n$ (**1**) and $[Zn_2(L)(Memal)_2(H_2O)_2]_n$ (**2-5**) [L = 4,4′-bipyridine (4,4′-bpy) (**2**), 1,2-bis(4-pyridyl)ethylene (bpe) (**3**), 1,2-bis(4-pyridyl)ethane (bpa) (**4**) and 4,4′-azobispyridine (azpy) (**5**), Scheme 1]. The crystal structure of **2** was reported previously [16a] and we only refer to it here for comparative purposes. Interestingly, **1** is quite different with respect to the related copper(II) complex [13a], the zinc(II) compound exhibiting an unusual three-dimensional (10,3)-d network. Complexes **2-5** are also 3D compounds where the corrugated layers of Zn(II)-methylmalonate are pillared by the rod-like L coligands.

2. Experimental

2.1. Materials and methods

Solvents and reagents utilized in the synthesis, except 4,4′-azobispyridine, were purchased from commercial sources and used without further purification. The azpy molecule was synthesized by means of the oxidation of 4-aminopyridine by a solution of sodium hypochlorite [21]. Compound **2** was prepared as previously described [16a]. Elemental analyses (C, H, N) were performed with an EA 1108 CHNS/0 automatic analyzer. Thermal analyses were carried out on a PerkinElmer system (mod. Pyris Diamond TG/DTA, SEGAI Service of the ULL-University) under a nitrogen atmosphere (with a flow rate of 80 $cm^3\,min^{-1}$) in the temperature range 25–950 °C. The samples (ca. 20 mg) were heated in a platinum crucible at a rate of 10 °C min^{-1}. The TG curves were analyzed as the