SYNTHESIS, STRUCTURE, AND THERMAL DECOMPOSITION OF A NOVEL ONE-DIMENSIONAL CHAIN COMPLEX OF MANGANESE(II) WITH 2,2′-DIPHENIC ACID AND 1,10-PHENANTHROLINE

Ren Yan-Wei,1 Dang Li-Long,2 Li Jun,1 Gao Wei-wei,1 and Zhang Feng-Xing1

A novel one-dimensional (1D) chain coordination polymer \([\text{Mn}_2(2,2′\text{-dipha})_2(\text{phen})]_n\) has been synthesized by hydrothermal reaction, and characterized by elemental analysis, IR spectroscopy, TGA, and X-ray diffraction. Orange crystals crystallized in the monoclinic system, space group \(C2/c\) with \(a = 19.393(7) \text{ Å}, b = 19.183(7) \text{ Å}, c = 19.729(7) \text{ Å}, \beta = 90.826(6)^\circ, V = 7338(5) \text{ Å}^3, Z = 8\). In the crystal structure, one manganese atom is six-coordinated with four carboxylate oxygen atoms from one pentadentate 2,2′-dipha ligand and two tetradentate 2,2′-dipha ligands, and with two nitrogen atoms of one phen ligand, giving a slightly distorted octahedral geometry. The other manganese atom is five-coordinated with five oxygen atoms from two tetradentate 2,2′-dipha ligands and two pentadentate 2,2′-dipha ligands and has a trigonal bipyramidal environment. The TGA curve shows that the compound is stable below 310°.

Keywords: hydrothermal synthesis; manganese (II) complex; 2,2′-diphenic acid; thermal decomposition.

1. INTRODUCTION

Rational design and synthesis of one-, two-, and three-dimensional (1D, 2D, 3D) coordination polymers is an attractive field of research due to their structural characteristics, such as diverse coordination modes, intriguing architecture and porosity, and also to their tremendous potential as catalysts [1] and luminescent [2-4] and magnetic materials [5-7]. 2,2′-Diphenic acid (2,2′-H₂dipha) is considered to be a building block for constructing coordination polymers because of its various coordination modes and high reactivity with \(d\) and \(f\) elements. A number of transition metal and rare earth coordination polymers with 2,2′-dipha as a bridging ligand have been reported [8-10]. The coordination modes of the 2,2′-dipha ligand in these polymeric complexes are shown in Scheme 1. The hydrothermal technique is well suited to the preparation of crystals of synthetic minerals, new inorganic materials, and organometal coordination polymers. Therefore we chose the 2,2′-dipha ligand and 1,10-phenanthroline (phen) as reactants to build multidimensional architectures by hydrothermal reaction. In this paper, we report the synthesis and structure of a novel one-dimensional chain manganese coordination polymer with a 2,2′-dipha ligand and phen ligand, together with IR spectral and thermal decomposition data.
2. EXPERIMENTAL

2.1. Materials

2,2'-Diphenic acid was synthesized as described elsewhere [11]. The other reagents were of analytical grade from commercial sources and were used without further purification.

2.2. Synthesis of [Mn₂(2,2'-dipha)(phen)]ₙ

2,2'-Diphenic acid (0.48 g, 2 mmol), NaOH (0.16 g, 4 mmol), and MnCl₂·2H₂O (0.16 g, 1 mmol) were dissolved in distilled water (12 ml). A solution of 1,10-phenanthroline (0.20 g, 1 mmol) in ethanol (2 ml) was added. The resulting mixture was stirred at room temperature for 30 min until a homogeneous solution was obtained. The mixture was placed in a Teflon liner of an autoclave, which was then sealed and heated to 160°C for 4 days. It was allowed to cool to room temperature and orange rectangular crystals were obtained by filtration, washed with water and ethanol, and then air-dried (yield 60%). Anal. calcd. for Mn₂C₄₀H₂₄N₂O₈: C, 62.33%; H, 3.12%; N, 3.64%, Found: C, 61.88%; H, 3.23%; N, 3.49%.

2.3. Physical Measurements

The infrared spectrum of the title complex was recorded with an Equinox55 spectrophotometer in the range 4000-400 cm⁻¹ using a powdered sample on a KBr plate. Elemental analysis was carried out using a Vario EL-III elemental analyzer. Thermogravimetric analysis was performed on a Netzsch STA 449C instrument with a heating rate of 10°C min⁻¹ in nitrogen.

2.4. X-Ray Structure Determination

The diffraction data were collected on a Bruker SMART APEX CCD area detector employing graphite monochromated MoKα radiation (λ = 0.71073 Å) with ϕ and ω scan modes. The sample selected for investigation had dimensions of 0.38×0.34×0.28 mm³. The intensities were corrected for Lorentz and polarization (Lp) effects, and an empirical absorption correction was applied based on a series of ψ scans. The structure was solved by direct methods, with subsequent difference Fourier syntheses; the number of unique data (Rint = 0.0417) used for structure solution was 6334. The final cycle of refinement finally converged to R₁ = 0.0442, wR₂ = 0.1034 for 473 variables. The non-hydrogen atoms were assigned anisotropic displacement parameters in the refinement. All calculations were carried out using the SHEXTL-97 program [12]. Crystal data are listed in Table 1. Selected bond lengths and angles are given in Table 2.

3. RESULTS AND DISCUSSION

3.1. IR Spectrum

The IR spectrum of the title complex displays characteristic strong bands at 1549 cm⁻¹ and 1392 cm⁻¹, indicative of the presence of uₘₜ(−CO₂) and uₜ(−CO₂) for the carboxylic group, respectively, which are finally confirmed by X-ray...