Inorganica Chimica Acta 426 (2015) 50–54

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

New coordination polymers with chromato bridges: $^{1}_{\infty}$[Ni(phen)$(H_2O)_2$(μ-O_2CrO_2)] and $^{3}_{\infty}$[Mn(4,4′-bipy)(H_2O)(μ-O_3CrO)]·H_2O

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ARTICLE INFO

Article history:
Received 8 October 2014
Received in revised form 17 November 2014
Accepted 19 November 2014
Available online 3 December 2014

Keywords:
Nickel complexes
Manganese complexes
Chromato ligands
Coordination polymers

ABSTRACT

Two new coordination polymers have been assembled using the chromato ions as bridging ligands: $^{1}_{\infty}$[Ni(phen)$(H_2O)_2$(μ-O_2CrO_2)] **1**, and $^{3}_{\infty}$[Mn(4,4′-bipy)(H_2O)(μ-O_3CrO)]·H_2O **2**. In crystal **1** the chromate ions act as bridges connecting two nickel ions through two oxygen atoms, resulting in infinite chains. 1,10-Phenanthroline acts as a blocking ligand. In compound **2**, each chromato ion is connected to three manganese ions, resulting in layers which are parallel to the *ab* plane. The layers are constructed from {Mn_3Cr_3} meshes, each metal atom being shared between three other meshes. The structure is expanded into the third direction by connecting the inorganic layers through 4,4′-bipy spacers. The thermal decomposition of the two compounds has been investigated.

1. Introduction

The chromate anion, CrO_4^{2-}, has a quite rich coordination chemistry. It can act as a terminal ligand, through one oxygen atom, or as a bridge, involving in the interaction with the metal ion two, three or all the oxygen atoms [1]. In the last cases, either oligonuclear complexes or coordination polymers can be assembled. The interest in this chemistry is due to several reasons: (i) chromium(VI) compounds are known to rise important ecological problems, showing a strong mutagenic effect [2]; (ii) the various bridging modes of the chromate anion affords coordination polymers with relevance in crystal engineering; (iii) some complexes of transition metal ions with chromato ligands are useful precursors for obtaining mixed metal oxides [3], or mixtures of oxides, which can be used as catalysts [4]. The chromato-bridged polynuclear complexes are assembled by reacting transition metal ions with a soluble chromate (usually of sodium, potassium, or ammonium) with or without additional chelating or bridging ligands. Generally, the chelating (blocking) ligands are employed to obtain discrete species and 1-D coordination polymers. For example, the reaction between the mononuclear complex [$LFeCl_3$] (L = 1,4,7-trimethyl-1,4,7-triazacyclononanine) and $(NH_4)_2CrO_4$ lead to a binuclear complexes with triple chromato bridges connecting the iron(III) ions [5]; a tetranuclear complex, [{Cu(2,2′-bipy)$_2$}$_3$(μ-CrO_4)]$(ClO_4)_4$·H_2O, has been obtained by reacting potassium chromate with copper(II) perchlorate and 2,2′-bipyridine, the chromato ion being linked to three copper(II) ions [6]. Interestingly, by replacing 2,2′-bipyridine with 1,10-phenanthroline, a binuclear complex [Cu(II)Cr(VI)] complex with monodentate chromate was obtained [7]. In principle, if only one bidentate chelating ligand or a macrocycle is attached to the assembling cation, the formation of 1-D coordination polymers is favored. A nice example is the chain resulted by connecting the {Ni(MAC)}$^{2+}$ complex cations with chromato bridges (MAC = 2,5,9,12-tetramethyl-1,4,8,11-tetraazacyclotetradecane) [8]. Conversely, 2-D and 3-D coordination polymers can be constructed using divergent (*exo*-dentate) ligands. One of the most popular bridging ligand in crystal engineering is 4,4′-bipyridine [9]. Herein we report on two new chromato-bridged coordination polymers, constructed using nickel(II) and manganese(II) as assembling cations, in the presence of 1,10-phenathroline (phen) and, respectively, 4,4′-bipyridine (4,4′-bipy).

2. Experimental part

2.1. Materials and physical measurements

Nickel(II) acetate tetrahydrate, manganese(II) acetate tetrahydrate, sodium chromate, 1,10-phenathroline monohydrate, and 4,4′-bipyridine were purchased from commercial sources and used as received. IR spectra (KBr pellets) were recorded on a BIO-RAD FTS 135 spectrophotometer from 4000 to 400 cm^{-1}. Diffuse reflectance

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http://dx.doi.org/10.1016/j.ica.2014.11.009
0020-1693/

UV–Vis spectra have been recorded on a Jasco V 670 spectrophotometer, using Spectralon as standard, in the range 300–1500 nm.

The heating curves (TG and DTA) were recorded using a Labsys 1200 SETARAM instrument, with a sample mass of 9–17 mg over the temperature range of 293–1173 K, using a heating rate of 10 K min^{-1}. The measurements were carried out in synthetic air atmosphere (flow rate 16.66 cm^3 min^{-1}) by using alumina crucibles.

2.2. Synthesis of [Ni(phen)(H_2O)$_2$(CrO_4)] **1**

To an aqueous solution (10 mL) of Ni(CH_3COO)$_2$·4H_2O (124.4 mg, 0.5 mmol) were added under continuous stirring Na_2CrO_4 (40.5 mg, 0.25 mmol) and 1,10-phenanthroline monohydrate (99.1 mg, 0.5 mmol). The solution was stirred for 30 min and the resulted greenish powder was filtered. Green single crystals appeared after several days by slow evaporation of the filtrate at room temperature. IR data (KBr, cm^{-1}): 726m, 773m, 877vs, 1109w, 1144w, 1341w, 1424m, 1517w, 1581w, 3008m.

2.3. Synthesis of [Mn(4,4′-bipy)(H_2O)(CrO_4)]·H_2O **2**

To an aqueous solution (10 mL) of Mn(CH_3COO)$_2$·4H_3O (122.5 mg, 0.5 mmol) were added under continuous stirring Na_2CrO_4 (40.5 mg, 0.25 mmol) and a solution of 4,4′-bipyridine (39 mg, 0.5 mmol) in 5 mL ethanol. The brown powder which precipitated overnight was filtered in the next day. Brown single crystals appeared after several days by slow evaporation of the filtrate at room temperature. IR data (KBr, cm^{-1}): 626m, 671w, 815m, 1043w, 1066w, 1219w, 1339vw, 1436s, 1487w, 1565s, 1599vs, 2925vw, 3042w, 3072vw, 3437w.

2.4. X-ray crystallography

Crystals were measured on a STOE IPDS II single crystal diffractometer using graphite-monochromated Mo Kα radiation. The structures were solved by direct methods and refined by full-matrix least-squares techniques based on F^2. All non-H atoms were refined anisotropically, and hydrogen atoms were introduced at calculated positions (riding model). A summary of the crystallographic data and the structure refinement for crystals **1** and **2** is given in Table 1.

Table 1
Crystallographic data, details of data collection and structure refinement parameters for compounds **1** and **2**.

Compound	1	2
Chemical formula	$C_{12}H_8CrN_2NiO_6$	$C_{20}H_{16}Cr_2Mn_2N_4O_{11}$
M (g mol^{-1})	386.89	702.55
T (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	monoclinic	orthorhombic
Space group	$C2/c$	Pnab
a (Å)	15.1209(3)	10.838(2)
b (Å)	14.2463(4)	11.0663(5)
c (Å)	6.7586(5)	21.8829(14)
β (°)	105.668(5)	90.00
V (Å^3)	1401.82(11)	2624.4(2)
Z	4	4
D_{calc} (g cm^{-3})	1.833	1.777
μ (mm^{-1})	2.148	1.810
F(000)	776	1400
Goodness-of-fit (GOF) on F^2	1.203	1.087
Final R_1, wR_2 [$I > 2\sigma(I)$]	0.0307, 0.0689	0.0433, 0.1100
R_1, wR_2 (all data)	0.0504, 0.0779	0.0526, 0.1100
Largest difference in peak and hole (e Å^{-3})	−0.409, 0.581	−0.831, 0.985

The powder X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance diffractometer with a nickel filtered Cu Kα1 radiation (λ = 1.5418 Å) in range of 10–100°, a step width of 0.02° and an acquisition time of 2 s per step.

3. Results and discussion

3.1. Description of the crystal structures

Two coordination polymers have been assembled using the chromate ion as a bridge: $^{1}_{\infty}$[Ni(phen)(H_2O)$_2$(μ-O_2CrO_2)] **1** and $^{3}_{\infty}$[Mn(4,4′-bipy)(H_2O)(μ-O_3CrO)]·H_2O **2**. The second compound is constructed using 4,4′-bipy as an additional bridge. Let us discuss first the crystal structure of **1**. The chromate ions act as bridges connecting through two oxygen atoms two nickel ions, resulting in infinite chains, running along the crystallographic *c* axis. (Fig. 1). The chromate oxygen atoms are located in *trans* positions to the nickel ion (Ni1–O1 = 2.120(2) Å). The nickel ion is located on a special position and shows a slightly elongated octahedral stereochemistry, the equatorial plane being formed by two nitrogen atoms arising from the phenanthroline molecule Ni1–N1 = 2.057(3) Å) and by two *cis* aqua ligands (Ni1–O3 = 2.061(2) Å). The Cr–O distances vary between 1.647(2) and 1.652(2) Å. The intrachain Ni···Cr and Ni···Ni distances are 3.511 and, respectively, 6.759 Å. This type of chain is expected to be general for complexes of general formula [M(AA)(H_2O)$_2$(μ-O_2XO_2)] where the tetrahedral dianions, XO_4^{2-}, act as bridges (AA = chelating ligand; X = S, Se). Indeed, compound **1** is isostructural with two [Zn(phen)(H_2O)$_2$(XO_4)] complexes (X = S [10], Se [11]). A similar architecture was observed for the copper-sulfate derivative, [Cu(bipy)(H_2O)$_2$(SO_4)] [12]. Moreover, the packing diagrams for these compounds and **1** are similar. Two types of forces are involved in sustaining the supramolecular architecture in the crystal (Fig. 2): (i) H-bond interactions between the aqua ligands from one chain and the chromato ligand from another one, resulting in double supramolecular chains (O2···O3 = 2.705 Å and O2···O3^{i} = 2.671 Å; ^{i} = x, 1 − y, 0.5 + z); (ii) π–π stacking interactions, involving the phen molecules, which connect double supramolecular chains, resulting in supramolecular layers (distances between 3.42 and 3.72 Å). The diffuse reflectance electronic spectrum of **1** exhibits the characteristic features for an octahedral nickel(II) ion [13], with

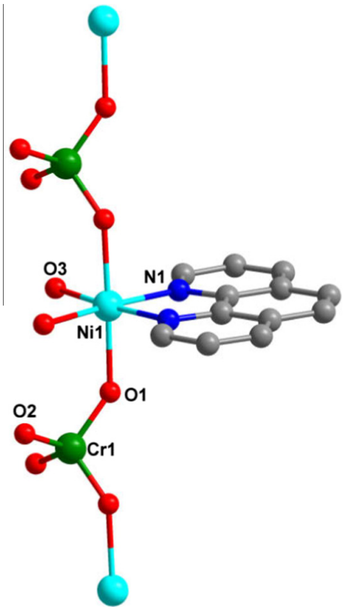

Fig. 1. View of the 1-D coordination polymer in crystal **1**, along with the atom numbering scheme.