Inorganica Chimica Acta 372 (2011) 286–294

Contents lists available at ScienceDirect

Inorganica Chimica Acta

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

Syntheses and structure of heterobimetallic helical polymeric Mo–M(II) (M = Mn, Co, Zn, Cd or Ni) complexes using a flexidentate metalloligand

Dibakar Deb, Manish Bhattacharjee *

Department of Chemistry, Indian Institute of Technology, Kharagpur 721302, India

ARTICLE INFO

Article history:
Available online 30 March 2011

Dedicated to Prof. S.S. Krishnamurthy on the occasion of his 70th birthday

Keywords:
Heterobimetallic
Metalloligand
Molybdenum
Polymeric
Helical

ABSTRACT

A series of heterobimetallic polymeric complexes of manganese, cobalt, zinc, cadmium and nickel, $[M(Mo_2O_5L_2)(MeOH)_2(H_2O)_2]_n{\cdot}nH_2O$ {M = Mn (**2**), $n = 1$, Co (**3**), $n = 0$, Zn (**4**), $n = 1$ and Cd (**5**), $n = 1$} and $[Ni(Mo_2O_5L_2)(MeOH)(H_2O)_3]_n{\cdot}2H_2O{\cdot}MeOH$ (**6**) have been synthesized form the reaction of $[\{Na_4(H_2O)_4(\mu\text{-}H_2O)_2\} \subset (Mo_2O_5L_2)_2]$ (**1**) {LH_2 = 2-(3,5-di-tert-butyl-2-hydroxybenzylamino)acetic acid} with the corresponding metal salts. The complexes have been structurally characterized. The Complexes, **3** and **6** undergo thermal decomposition to afford mixed oxides of the type, $MMoO_4{\cdot}MoO_3$ {M = Co or Ni}.

1. Introduction

Heterobimetallic and multimetallic mixed oxides are important materials. Some of these have unique catalytic activities, ferroelectric, magnetic, and optical properties [1–6]. For example, various combination of mixed oxides of cobalt, nickel, and molybdenum on solid support have been used as catalysts for hydrodesulphurization [7–11] and hydrodenitrogenation in petroleum industries [12,13]. In the traditional solid state synthesis of such mixed metal oxides, high temperature is required and control over the composition of the mixed metal oxides is very difficult [14–16]. Use of discrete heterobimetallic complexes as single source precursors are gaining importance over last few years [14–16]. Synthesis of heterobimetallic or heterotrimetallic complexes still remains a challenge. It may be noted that, it is very difficult to control the synthesis of heterometallic complexes using reaction between mixture of metal salts and organic ligands, as there is always a probability of the formation of homometallic complexes. One of the best routes to such complexes is the reaction of a preformed metal complex having free Lewis basic site, known as metalloligand, with another Lewis acidic metal [14–18]. In this approach, the side reaction is minimum and exclusively heterobimetallic complexes can be obtained.

Over last few years a lot of effort has gone into the synthesis of transition metal helicates because of their importance in supramolecular chemistry [19–21] As a part of our on-going program, we have recently reported synthesis and structure of cobalt [22] and nickel [23] complexes of a molybdenum metalloligand, $[MoO_2L]^-$ {L = carboxymethyl-(3,5-di-tert-butyl-2-hydroxy-benzyl)aminoacetate}, which were found to form hydrogen bonded helical chains in solid state. Apart from these we have recently reported synthesis and structures of sodium [24], potassium [25] and lithium [26] complexes of another metalloligand, $[MoO_3L]^{2-}$ {LH_2 = iminodiacetic acid}. We have also reported synthesis and structure of a binuclear molybdenum metalloligand, $[Mo_2O_5L_2]^{2-}$ [LH_2 = 2-(3,5-di-tert-butyl-2-hydroxybenzylamino)acetic acid] and its sodium and cesium complexes [27]. Here in we report synthesis and structure of manganese, cobalt, zinc, cadmium and nickel complexes, of the metalloligand, $[Mo_2O_5L_2]^{2-}$ [LH_2 = 2-(3,5-di-tert-butyl-2-hydroxybenzylamino)acetic acid].

2. Experimental

2.1. Materials

2,4-Di-*tert*-butyl phenol was purchased from Fluka. Glycine, formaldehyde, $Na_2MoO_4{\cdot}2H_2O$ and solvents used were reagent grade products. The ligand, 2-(3,5-di-tert-butyl-2-hydroxybenzylamino)acetic acid and $[\{Na_4(H_2O)_4(\mu\text{-}H_2O)_2\} \subset (Mo_2O_5L_2)_2]$ (**1**) were synthesized by the method reported earlier form this laboratory [27].

---

* Corresponding author.
E-mail address: mxb@iitkgp.ac.in (M. Bhattacharjee).

0020-1693/$ - see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2011.03.036

2.2. Physical measurements

Elemental analyses were performed using Perkin–Elmer C, H, N, analyzer model 2400. The ^1H NMR spectra of the ligand were recorded in CD_3OD on a Bruker Avance II 400 MHz instrument. The IR spectra were recorded on a Parkin–Elmer model 883 spectrometer. UV–Vis spectra were recorded in solution in a Shimadzu model UV-1601 spectrophotometer. Powder X-ray diffraction (XRD) was done by using Cu Kα radiation on a Mini Flex Rigaku X-ray diffractometer. Thermo gravimetric analyses were performed on a Perkin–Elmer Diamond Pyris TG/DTA analyzer under oxygen atmosphere.

Synthesis of $[M(Mo_2O_5L_2)(MeOH)_2(H_2O)_2]_n{\cdot}nH_2O$ {M = Mn (**2**), $n = 1$, Co (**3**), $n = 0$, Zn (**4**), $n = 1$ and Cd (**5**), $n = 1$} and $[Ni(Mo_2O_5L_2)(MeOH)(H_2O)_3]_n{\cdot}2H_2O{\cdot}MeOH$ (**6**).

To an aqueous methanolic solution (40 cm^3) of 1 (0.955 g, 0.5 mmol) was added to an aqueous solution of $MCl_2{\cdot}nH_2O$ {M = Mn, $n = 4$; M = Co, Ni, Zn, $n = 6$} or $Cd(NO_3)_2{\cdot}4H_2O$ (1 mmol) and the reaction solution was stirred for about 1 h, whereupon the color of the reaction solution changed form yellow to red. The reaction solution was filtered and the filtrate afforded crystalline product upon standing for 1–2 weeks.

Yield: 0.698 g (68%). *Anal.* Calc. for **2**, $C_{36}H_{64}Mn_1Mo_2N_2O_{16}$ (Mol wt.: 1027.72): C, 42.07; H, 6.28; N, 2.73. Found: C, 41.89; H, 5.95; N, 2.45%. Yield: 0.598 g (59%). *Anal.* Calc. for **3**, $C_{36}H_{62}Co_1Mo_2N_2O_{15}$ (Mol wt.: 1013.7): C, 42.65; H, 6.16; N, 2.76. Found: C, 42.42; H, 5.93; N, 2.40%. Yield: 0.560 g (54%). *Anal.* Calc. for **4**, $C_{36}H_{64}Zn_1Mo_2N_2O_{16}$ (Mol wt.: 1038.17): C, 41.65; H, 6.21; N, 2.70. Found: C, 41.26; H, 5.96; N, 2.32%. Yield: 0.553 g (51%). *Anal.* Calc. for 5, $C_{36}H_{64}Cd_1Mo_2N_2O_{16}$ (Mol wt.: 1085.19): C, 39.84; H, 5.94; N, 2.58. Found: C, 39.63; H, 6.02; N, 2.86%. Yield: 0.758 g (71%). *Anal.* Calc. for **6**, $C_{36}H_{68}Ni_1Mo_2N_2O_{18}$ (Mol wt.: 1067.5): C, 40.50; H, 6.42; N, 2.62. Found: C, 40.21; H, 6.75; N, 2.83%.

2.3. Thermal decomposition of **3** and **6**

Compounds **3** and **6** were heated in a muffle furnace at a ramping rate of 4 °C/min to 700 °C from room temperature and were heated at 700 °C for 4 h in air. The samples were cooled to room temperature. Compound **3** afforded deep black-violets solid product which on grinding gave a green solid. However, compound **6** afforded a greenish-yellow solid, and the color remained same on grinding.

2.4. Crystal structure determination

Suitable crystals of all the compounds were grown from MeOH/water reaction solution, at room temperature over a period of 7 to 15 days. The single crystal data were collected on Bruker Smart APEX system that uses graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods and refined by least square methods on F^2 employing WINGX [28] package and the relevant programs (SHELX-97 [29] and ORTEP-3 [30]) implemented therein. No absorption corrections were used for **2**, **4**, **5** and **6**. An empirical absorption correction was applied for **3** [31]. For the complex **3** final refinement was done by using PLATON squeeze option [32].

Non-hydrogen atoms were refined anisotropically and hydrogen atoms on C-atoms were fixed at calculated positions and refined using a riding model. Whereas the H-atoms on water molecules in all the compounds could not be located, the N–H protons could be located only in the cases of compounds **2**, **3** and **5**. The details of crystal data are given in Table 1. Important bond distances and bond angles are given in Table 2.

3. Results and discussion

3.1. Synthesis and characterization of the complexes **2**, **3**, **4**, **5**, and **6**

The bimetallic complexes, **2**–**6**, were synthesized from reactions of compound **1** with the metal chloride or nitrate (Cd) in aqueous methanol.

The elemental analyses agree well with the compositions. The compounds were further characterized by IR, UV–Vis, and ^1H (compounds **4** and **5**) NMR spectroscopy. The IR spectra of the compounds show two sharp bands at *ca* 920 and *ca* 880 cm^{-1} due to symmetric and antisymmetric *cis*-$Mo{=}(O)_2$ stretch and a band at *ca* 780 cm^{-1} due to Mo–O–Mo stretch and thus clearly shows the presence of $[MoO_2(\mu\text{-}O)MoO_2]$ moiety. In addition the IR spectra of the compounds show a strong band at *ca* 1600 cm^{-1} due to molybdenum bonded carboxylate stretching. The UV–Vis spectra of the compounds show strong bands due to ligand to metal charge transfer transition at *ca* 350 nm along with the ligand internal transitions at *ca* 260 and at *ca* 220 nm.

The ^1H (d^4 MeOH) NMR spectra of **4** and **5** show signals at *ca* 1.19 (s, 9H) and *ca* 1.40 (s, 9H) due to methyl protons of the *t*-butyl groups. The CH_2 proton signals appear at *ca* 3.36 (br; 2H) and *ca* 4.25 (br; 2H) ppm. The signal at *ca* 4.80 (br; 1H) ppm can be assigned to NH proton. We could not observe the signals due to protons of coordinated water. This may be due to excessive broadening of the signals. The signals for the aromatic protons appear at *ca* 6.85 (br. 1H) and *ca* 7.10 (br; 1H) ppm. Thus, ^1H NMR spectra clearly shows that, the ligand remains coordinated to the molybdenum centers in solution.

3.2. Crystal structure of $[Mn(Mo_2O_5L_2)(MeOH)_2(H_2O)_2]_n{\cdot}H_2O$ (**2**) and $[Cd(Mo_2O_5L_2)(MeOH)_2(H_2O)_2]_n{\cdot}H_2O$ (**5**)

Compounds **2** and **5** are isostructural and crystallize in triclinic space group $P\bar{1}$ and the asymmetric unit contains two metal ions [Mn(II) or Cd(II)], each with half occupancy, one metalloligand, one water molecule coordinated to one of the manganese/cadmium ions, two methanol coordinated to each manganese/cadmium, and one water molecule of crystallization (Fig. 1a and b). The water of crystallization in compound **2** is disordered. Since the compounds are isostructural, the structural features of compound **2** are described below.

The structure of the molybdenum metalloligand is same as observed in the case of compound **1**. The bond distance are similar to that observed in compound **1** [27]. Both the manganese centers in compound **2** are in octahedral coordination environment as evidenced by the *trans*-∠O–Mn–O bond angles, which were found to be 180°. The coordination environments of the two manganese centers are slightly different.

One of the manganese centers, Mn1, is coordinated to two symmetrically equivalent Mo = O oxygens, O8 and $O8^{\#1}$ ($\#1 = -x + 2, -y + 1, -z$), from two metalloligands, two symmetrically equivalent carboxylate oxygens, O6 and $O6^{a}$, from two metalloligands, and two symmetrically equivalent methanol oxygens, O12 and $O12^{\#1}$ ($\#1 = -x + 2, -y + 1, -z$). The other manganese center, Mn2 is coordinated to two symmetrically equivalent carboxylate oxygens, O11 and $O11^{\#2}$ ($\#2 = -x + 2, -y, -z$), two symmetrically equivalent methanol oxygens, O13 and $O13^{\#2}$ ($\#2 = -x + 2, -y, -z$), and two symmetrically equivalent water oxygens, O1W and $O1W^{\#2}$ ($\#2 = -x + 2, -y, -z$), oxygens. Thus, each metalloligand bridges two manganese centers via two carboxylate oxygens, O6 and O11 and a helical polymeric 1D chain is formed. One helical pitch comprises of three Mn centers and two metalloligands and the pitch length is equal to the crystallographic *b* axis (11.6728 Å). The molecule has hydrogen bond donor as well as acceptor sites and in the