



# Synthesis and characterisation of Co–Mo complexes containing the $[\text{Co}(\text{C}_2\text{H}_8\text{N}_2)_3]^{2+}$ cation and $[\text{Mo}_2\text{O}_7\text{L}]^{4-}$ anion, where L is an oxalic, tartaric, citric or nitrilotriacetic acid residue

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## ARTICLE INFO

### Article history:

Received 25 May 2012

Accepted 8 August 2012

Available online 24 August 2012

### Keywords:

Cobalt  
Molybdenum  
Oxalate  
Citrate  
Tartrate  
NTA

## ABSTRACT

A set of bimetallic Co–Mo complexes has been synthesised in yields of approximately 95% by the sequential dissolution of ethylenediamine, different  $\text{Co}^{2+}$  carboxylates and ammonium heptamolybdate in water. Data collected from elemental analysis, XRD, UV–Vis, IR, Raman, XPS, and EXAFS spectroscopy suggest that all of the complexes have similar structures that correspond to the general formula of  $\text{NH}_4(\text{enH}_2)_x[\text{Co}(\text{en})_3][\text{Mo}_2\text{O}_7\text{L}]\cdot\text{H}_2\text{O}$ , where L is oxalic, tartaric, citric or nitrilotriacetic acid residue. A special feature of the complexes is the presence of two different molybdenum atoms linked together by an oxygen bridge in an octahedral and tetrahedral oxygen environment, as well as a cobalt 2+ atom that is in an octahedral environment with the nitrogen atoms of the ethylenediamine.

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## 1. Introduction

Different bimetallic Co–Mo complex compounds are used in the preparation of supported hydrotreating catalysts [1–6]. These complexes have several important properties: (1) the Co/Mo atomic ratio is close to 1/2, as seen in the catalyst's active component; (2) the metal atoms in the molecule are close in proximity to each other; (3) the presence of the carboxylic ligands acts to screen active metals from undesirable chemical interactions with the support; (4) the complexes are easy to synthesise, highly water soluble and stable under the conditions for catalyst preparation; and (5) crystallisation does not occur during storage or evaporation of the solutions. One of the compounds that meets most of these requirements is  $\text{NH}_4(\text{enH}_2)_{0.5}[\text{Co}(\text{en})_3][\text{Mo}_2\text{O}_7\text{C}_2\text{O}_4]\cdot\text{H}_2\text{O}$ , as described in [7]. The complex, subsequently designated as CoMoOxRef, consists of the  $[\text{Co}(\text{en})_3]^{2+}$  fragment, in which the  $\text{Co}^{2+}$  cation is in an octahedral environment with the nitrogen atoms of the ethylenediamine, coordinated to the  $[\text{Mo}_2\text{O}_7\text{C}_2\text{O}_4]^{4-}$  anion, that consists of two molybdenum-containing fragments in an octahedral and tetrahedral oxygen environment linked through a single oxygen bridge. The main inadequacy of the complex is its complicated

hydrothermal synthesis. In addition, the complex crystallises during long-term storage, and formation of the coarse-dispersion active component could occur while the catalyst, obtained from a complex supported on porous  $\text{Al}_2\text{O}_3$ , is dried. Previously, we found that bimetallic Co–Mo complexes containing citrate ligands do not crystallise from solution during storage or drying [6]. Hydrotreating catalysts prepared from these complexes have a high degree of active component dispersion [5]. In fact, the citrate ligands screen cobalt and molybdenum from an undesirable interaction with  $\text{Al}_2\text{O}_3$ , which leads to the complete sulfidation of the active component [8].

The aim of this work is to develop a simple method for the synthesis of bimetallic Co–Mo complex compounds with structures similar to those of the CoMoOxRef complex that utilise citric, tartaric or nitrilotriacetic acid residues as the ligands coordinated to the molybdenum atom in an octahedral oxygen environment. The complexes obtained were studied by UV–Vis, IR, Raman, XPS, and EXAFS spectroscopy. Then, these complexes were used for the preparation of supported hydrotreating catalysts.

The substitution of oxalic acid in the CoMoOxRef composition by other carboxylic acids with preservation of the complex structure allows us to illustrate the influence of different ligands on properties of obtained sulfide hydrotreating catalysts in contrast to research works that are directed to the investigation of the various chelating ligands influence with using complexes of different structure.

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## 2. Experimental

### 2.1. Synthesis of the complexes

Reagents produced by Sigma–Aldrich (ammonium heptamolybdate tetrahydrate,  $((\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O})$  (ACS reagent), cobalt (II) oxalate dihydrate ( $\text{CoC}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ ), cobalt (II) hydroxide ( $\text{Co}(\text{OH})_2$ , 95%), citric acid ( $\text{C}_6\text{H}_8\text{O}_7$ , 98%), tartaric acid ( $\text{C}_4\text{H}_6\text{O}_6$ , 99%), nitrilotriacetic acid ( $\text{C}_6\text{H}_9\text{NO}_6$ , >98%), and ethylenediamine ( $\text{C}_2\text{H}_8\text{N}_2$ , 99%) and by Alfa Aesar (cobalt (II) citrate dehydrate,  $(\text{Co}_3(\text{C}_6\text{H}_5\text{O}_7)_2\cdot 2\text{H}_2\text{O}$ , 98%)) were used for the complex preparation.

Cobalt tartrate ( $\text{CoC}_4\text{H}_4\text{O}_6\cdot 2.5\text{H}_2\text{O}$ ) and cobalt nitrilotriacetate ( $\text{Co}_3(\text{C}_6\text{H}_6\text{NO}_6)_2\cdot 3\text{H}_2\text{O}$ ) were synthesised using  $\text{Co}(\text{OH})_2$ , tartaric and nitrilotriacetic acids, according to the techniques described in [9,10].

Unfortunately, the accuracy of the elemental analysis and other investigation methods used below did not allow us to determine the precise number of water molecules included in the complexes' structures.

For some complex compounds the TGA method can be used for determination of crystallised water amount that is removed from complexes at 50–150 °C [11,12]. In our case it is not possible since a monotonous weight loss 7–10% in this temperature range was pointed out for all the synthesised complexes that is specified by ammonium and partially ethylenediamine removal besides water removal [13].

Therefore, based on the data from [7], we assumed that each complex contained one molecule of water. However, in general, this assumption does not influence the complex's composition.

### 2.2. Synthesis of $\text{NH}_4(\text{enH}_2)_{0.5}[\text{Co}(\text{en})_3][\text{Mo}_2\text{O}_7\text{C}_2\text{O}_4]\cdot \text{H}_2\text{O}$

Ethylenediamine, cobalt oxalate and ammonium heptamolybdate, whose concentrations in a dark brown transparent solution were 2.282, 0.652 and 0.186 M, respectively, were sequentially diluted while stirred at room temperature. The pH of the final solution was 8.7. Then, 100 ml of the solution was prepared, and 10 ml was separated to obtain the UV–Vis spectrum. Then, 500 ml of ethanol was added to the remaining 90 ml of solution while stirring. An orange precipitate was obtained (subsequently designated as CoMoOx) and separated by filtration; it was then washed with ethanol and dried in a drying box. The yield was 96%. *Anal. Calc.* for  $\text{CoMo}_2\text{N}_8\text{C}_9\text{O}_{12}\text{H}_{35}$ : Mo, 27.5; Co, 8.5; N, 16.1; C, 15.5; H, 5.0. Found: Mo, 26.8; Co, 8.7; N, 15.6; C, 16.0; H, 4.8%.

### 2.3. Synthesis of $\text{NH}_4(\text{enH}_2)[\text{Co}(\text{en})_3][\text{Mo}_2\text{O}_7\text{C}_6\text{H}_5\text{O}_7]\cdot \text{H}_2\text{O}$

The synthesis and extraction of the complex, subsequently designated as CoMoCitr, were carried out in a similar manner to that of the CoMoOx synthesis, except that the concentrations of ethylenediamine, cobalt citrate and ammonium heptamolybdate were 2.604, 0.217 and 0.186 M, respectively. In addition, to provide the necessary ratios of the components, 0.217 M citric acid was added to the solution after the addition of cobalt citrate. The pH of the final solution was 7.8. The yield was 95%. *Anal. Calc.* for  $\text{CoMo}_2\text{N}_9\text{C}_{14}\text{O}_{15}\text{H}_{45}$ : Mo, 23.1; Co, 7.1; N, 15.2; C, 20.2; H, 5.4. Found: Mo, 22.7; Co, 7.1; N, 14.8; C, 20.6; H, 5.6%.

### 2.4. Synthesis of $\text{NH}_4(\text{enH}_2)_{0.5}[\text{Co}(\text{en})_3][\text{Mo}_2\text{O}_7\text{C}_4\text{H}_4\text{O}_6]\cdot \text{H}_2\text{O}$

The synthesis and extraction of the complex, subsequently designated as CoMoTart, were carried out in a similar manner to that of the CoMoOx synthesis, except that the concentrations of ethylenediamine, cobalt tartrate and ammonium heptamolybdate were 2.608, 0.652 and 0.186 M, respectively. The pH of the final solution

was 9.7. The yield was 94%. *Anal. Calc.* for  $\text{CoMo}_2\text{N}_8\text{C}_{11}\text{O}_{14}\text{H}_{39}$ : Mo, 25.3; Co, 7.8; N, 14.8; C, 17.4; H, 5.2. Found: Mo, 24.4; Co, 7.6; N, 14.5; C, 17.0; H, 4.9%.

### 2.5. Synthesis of $\text{NH}_4(\text{enH}_2)[\text{Co}(\text{en})_3][\text{Mo}_2\text{O}_7\text{NC}_6\text{H}_6\text{O}_6]\cdot \text{H}_2\text{O}$

The synthesis and extraction of the complex, subsequently designated as CoMoNTA, were carried out in a similar manner to that of the CoMoCitr synthesis, except that the concentrations of ethylenediamine, cobalt nitrilotriacetate, nitrilotriacetic acid and ammonium heptamolybdate were 2.608, 0.217, 0.217 and 0.186 M, respectively. The pH of the final solution was 10.4. The yield was 95%. *Anal. Calc.* for  $\text{CoMo}_2\text{N}_{10}\text{C}_{14}\text{O}_{14}\text{H}_{46}$ : Mo, 23.2; Co, 7.1; N, 16.9; C, 20.3; H, 5.5. Found: Mo, 22.9; Co, 7.1; N, 16.2; C, 21.1; H, 5.3%.

### 2.6. Investigation techniques

X-ray diffraction (XRD) was carried out using a HCG 4-C diffractometer (Freiberger Präzisionsmechanik, Germany) equipped with a copper anode ( $\text{Cu K}\alpha$ ) with a wavelength of 1.54 Å.

UV–Vis spectra were recorded by a Shimadzu UV-2501 PC spectrophotometer equipped with a diffuse reflection attachment, ISR-240 A. Spectra were registered against a  $\text{BaSO}_4$  reflection reference in the range of 11 000–53 000  $\text{cm}^{-1}$ .

HCNS analysis was carried out using a Vario EL III elemental analyser (ELEMENTAR Analysensysteme GmbH)

IR spectra were registered by a BOMEM MB-102 Fourier-transform IR spectrometer in the frequency range of 4000–250  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$ .

Raman spectra were recorded in the frequency range of 3600–100  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$  by a RFS 100/S BRUKER Raman spectrometer (Germany). An Nd-YAG laser line centred at 1064 nm with 100–450 mW of power was used as the excitation source.

EXAFS spectra were recorded at the Mo K-edge and Co K-edge in transmission mode at the EXAFS Station of the Siberian Synchrotron Radiation Centre (Novosibirsk). The VEPP-3 storage ring with an electron beam energy of 2 GeV and an average stored current of 100 mA was used as the source of radiation. The model curve simulations were performed by the VIPER code. The FEFF702 program was employed to fit the parameters of scattering. Samples were prepared for analysis to obtain an absorption jump value for Mo about 0.8 and for Co in the range of 0.2–0.8.

Investigation of the samples by XPS was carried out with a SPECS PHOIBOS 150 (Germany) electron spectrometer using non-monochromatic  $\text{Al K}\alpha$  ( $h\nu = 1486.6$  eV, 200 W). The binding energy scale (eV) was preliminarily calibrated by the position of the  $\text{Au}4f_{7/2}$  (84.0 eV) and  $\text{Cu}2p_{3/2}$  (932.6 eV) peaks. To minimize the effect of charging that arises in the process of photoemission, samples were spread on the double-sided adhesive tape. An electron flood gun was not used to compensate for charging.

## 3. Results and discussion

All complexes extracted from the solutions were orange-coloured with differing intensities. It should be noted that after the addition of ethanol to the CoMoOx solution a free-flowing crystallised precipitate was formed. In all other cases, adhesive precipitates were obtained that became free-flowing only after they were dried at room temperature during the day and ground in a mortar.

The X-ray diffraction pattern of the complex revealed a set of peaks at locations that coincide completely with those theoretically calculated from the structural data for CoMoOxRef (Fig. 1),

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