

ORIGINAL RESEARCH PAPER

SYNTHESIS AND INFRARED STUDY OF SOME NEW MOLYBDATO AND HYDROGENOMOLYBDATO ADDUCTS AND COMPLEXES OF COBALT, ZINC, ANTIMONY AND CADMIUM CHLORIDES

Serigne Fallou Pouye¹, Ibrahima Cissé^{1*}, Libasse Diop¹,
Lamine A. Diop²

¹*Université Cheikh Anta Diop, Faculté des Sciences et Techniques,
Département de Chimie, Laboratoire de Chimie Minérale et Analytique
(LACHIMIA), Dakar, Sénégal*

²*Saint Boniface College, Département de Chimie Organique,
Saint Boniface, Winnipeg, Canada*

*Corresponding author: icisse50@yahoo.fr

Received: August 24, 2012

Accepted: May, 17, 2013

Abstract: Five new molybdate (four) and hydrogenomolybdate (one) adducts and complexes have been synthesized and studied by infrared spectroscopy. The suggested structures are all discrete, the molybdate anion behaving as a trichelating, a monochelating, a bridging, a tetrachelating and a bichelating ligand. The environment around Zn, Co, Cd is tetrahedral or trigonal bipyramidal also for Zn - while being octahedral for Sb. The Cd pentanuclear adduct has a two metallic components structure, a tetranuclear anionic one with a tetrachelating molybdate, the second being a neutral dehydrated adduct component. The suggested structure for the hydrogenomolybdate adduct is discrete, the hydrogenomolybdate being present as a hydrogen bonded dimer behaves as a bridging bidentate ligand. The water molecules can be considered as a coordinating ligand or lattice. When secondary interactions through hydrogen bonds involving the water molecules are considered supramolecular architectures are obtained.

Keywords: *dimeric structure, discrete structures, H bonds, mono-, di-, tri- and tetrachelating molybdate, monocoordinating [MoO₄H], supramolecular architecture, two and three anionic components*

INTRODUCTION

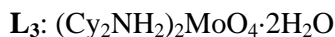
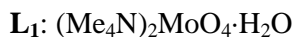
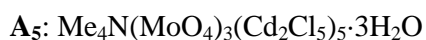
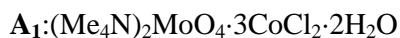
Hathaway has summarized the main results on the coordinating behavior of tetrahedral anions [1] but those concerning the molybdate and the hydrogenomolybdate anions were very scarce compared to those of the sulphate and oxalate anions. Our group which is interested in the coordinating ability of tetrahedral oxyanions since decades has published several papers dealing with the molybdate and hydrogenomolybdate anions [2-4]. We initiate here the study of the interactions between $(\text{Me}_4\text{N})_2\text{MoO}_4 \cdot \text{H}_2\text{O}$, $\text{Me}_4\text{NHMoO}_4 \cdot 2\text{H}_2\text{O}$ or $(\text{Cy}_2\text{NH}_2)_2\text{MoO}_4 \cdot \text{H}_2\text{O}$ with CoCl_2 , ZnCl_2 , CdCl_2 or SbCl_5 which has yielded five new molybdate and hydrogenomolybdate adducts and complexes. The infrared studies of the compounds have been carried out and structures suggested on the basis of these spectroscopic data.

EXPERIMENTAL

$(\text{Me}_4\text{N})_2\text{MoO}_4 \cdot \text{H}_2\text{O}$, $\text{Me}_4\text{NHMoO}_4 \cdot 2\text{H}_2\text{O}$ and $(\text{Cy}_2\text{NH}_2)_2\text{MoO}_4 \cdot \text{H}_2\text{O}$ have been obtained as described in [2, 3]. All the studied adducts have been obtained as precipitates (stirred around two hours) on mixing both ethanolic solutions of the molybdate salt - $(\text{Me}_4\text{N})_2\text{MoO}_4 \cdot \text{H}_2\text{O}$, $\text{Me}_4\text{NHMoO}_4 \cdot 2\text{H}_2\text{O}$ or $(\text{Cy}_2\text{NH}_2)_2\text{MoO}_4 \cdot \text{H}_2\text{O}$ - with the halide in specific ratios. The analytical data % calculated (% found) with the ratios salt/ MCl_2 (M = Co, Zn, Cd) or SbCl_5 reported below (Table 1) have allowed to suggest the following formulae.

Table 1. Analytical data of synthesized compounds

Compounds	Salt	Ratio (Salt/ MX_n)	% cal. (% found)
A ₁	L ₁	3/1	C = 13.05 (13.09); H = 3.82 (3.85); N = 3.79 (3.82)
A ₂	L ₂	2/1	C = 10.68 (10.63); H = 3.10 (3.19); N = 1.92 (1.89)
A ₃	L ₂	1/1	C = 8.47 (8.28); H = 3.00 (2.94); N = 2.47 (2.74)
A ₄	L ₃	1/1	C = 28.80 (28.09); H = 5.04 (5.25); N = 2.80 (3.03)
A ₅	L ₁	4/1	C = 2.04 (2.14); H = 0.77 (0.90); N = 0.60 (0.64)



The compounds A₂, A₄ and A₅ are white, A₃ green and A₁ blue.

The elemental analyses were performed at the laboratory of Microanalyses at the University of Bath (UK).

The infrared spectra were recorded by a Bruker FTIR spectrometer at the College of Saint Boniface-Winnipeg (Canada), the sample being as KBr pellets. The IR data are given in cm^{-1} [abbreviations: (vs) very strong, (s) strong, (m) medium, (sh) shoulder]. All the chemicals were purchased from Aldrich Chemical Company and were used without any further purification.

RESULTS AND DISCUSSION

Let us consider the IR data of the studied adducts and complexes.

Table 2. IR main data of the compounds A_1 - A_5

Compounds	Assignments	
A_1	906 m	782 s; 694 vs
A_2	900 m	877 m; 820 sh; 693 vs
A_3	911 s	843 m; 715 m
A_4	-----	820 sh ; 830 sh; 730 vs
A_5	-----	860 sh; 740 vs; 720 s; 690 s; 668 s

$A_1: (\text{Me}_4\text{N})_2\text{MoO}_4 \cdot 3\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$

From these data, we suggest a discrete structure with a trichelating molybdate for A_1 (Figure 1).

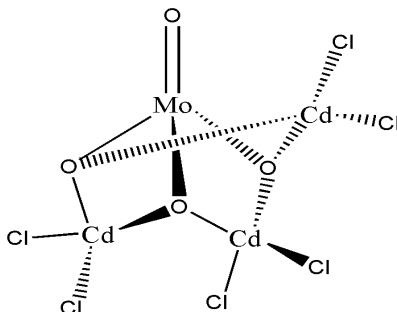


Figure 1. Proposed structure for A_1

$A_2: (\text{Me}_4\text{N})_2\text{MoO}_4 \cdot \text{ZnCl}_2 \cdot \text{H}_2\text{O}$

According to the fact that the water molecules are considered as coordinating ligand or lattice, being involved in hydrogen bonding or lattice, the three structures can be suggested for A_2 :

- a monomeric structure where water molecules are considered as lattice (Figure 2a);
- a dimeric structure with coordinating water molecules (Figure 2b);
- a dimeric structure with bridging water molecules (Figure 2c).

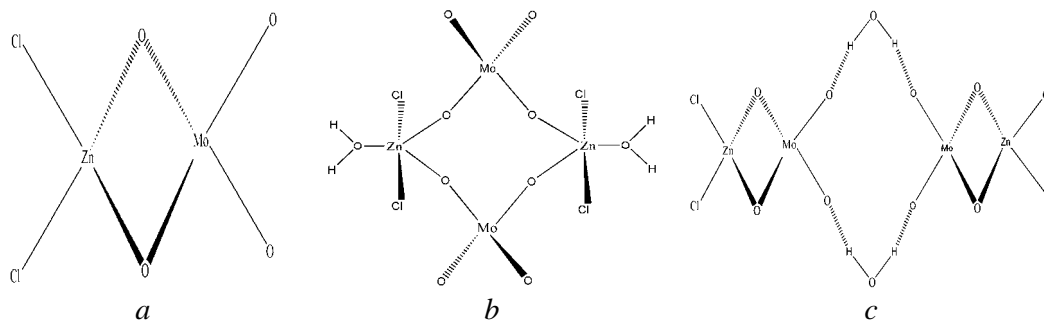


Figure 2. Proposed structures for A_2

A_3 : $(Me_4N)HMoO_4 \cdot SbCl_5 \cdot 2H_2O$

While considering the water molecules coordinated or lattice, two dimeric structures are possible for A_3 :

- a structure with an acetic acid hydrogen bonded type linking the hydrogenomolybdate anions in a dimer, the anion being a monocoordinating ligand, the water molecules being lattice (Figure 3a);
- a second structure with an acetic acid hydrogen bonded type linking the hydrogenomolybdate anions linked through $OH \cdots O$ hydrogen bonds to two $H_2O \cdot SbCl_5$ adducts (Figure 3b).

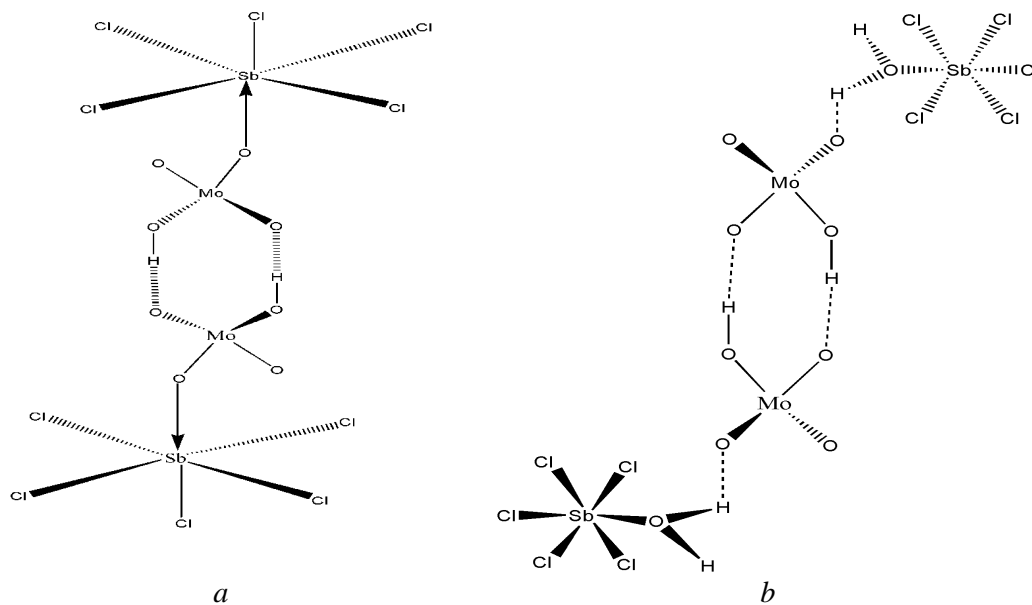


Figure 3. Proposed structures for A_3

A_4 : $(Cy_2NH_2)_2MoO_4 \cdot 5CdCl_2 \cdot 2H_2O$

A discrete two metallic components structure with a tetrachelating molybdate in the tetranuclear metallic component, the second metallic component being $CdCl_2 \cdot 2H_2O$ can be suggested for A_4 (Figure 4). The tetranuclear component dimerizes with the involvement of the cations through hydrogen bonds leading to the cage structure. When

OH....Cl intermolecular hydrogen bonds are considered a supramolecular architecture is obtained.

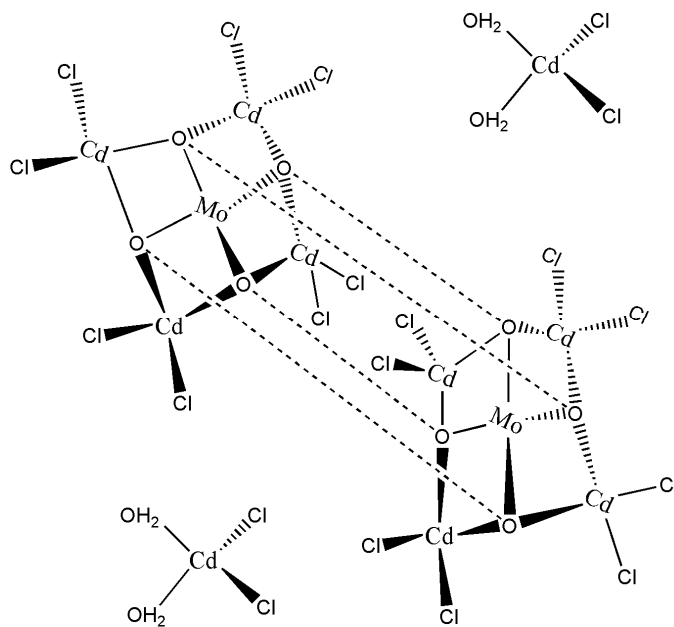


Figure 4. Proposed structure for A_4

A_5 : $\text{Me}_4\text{N}(\text{MoO}_4)_3(\text{Cd}_2\text{Cl}_5)_3 \cdot 3\text{H}_2\text{O}$

A three metallic anionic components structure with two similar ones containing a bichelating molybdate and one containing a monochelating molybdate, with these three anionic components interacting electrostatically with the tetramethylammonium ions is proposed for A_5 (Figure 5).

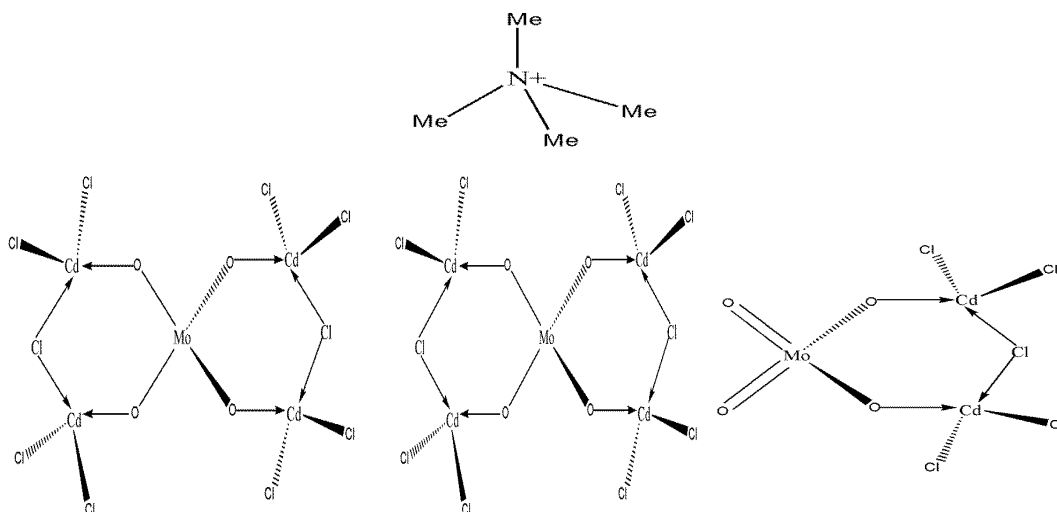


Figure 5. Proposed structure for A_5

In this complex, the formation of $[\text{Cd}_2\text{Cl}_5]^-$ binuclear complex in situ is worthy.

Me_4N^+ is involved in electrostatic interactions with the anionic components in A_1 , A_2 , A_3 and A_5 .

CONCLUSION

The studied adducts and complexes have discrete structures (monomers, dimers, a two metallic or a three components one) with a mono-, di-, tri-, tetrachelating molybdate and a monocoordinating hydrogenomolybdate. In the case of the compound containing dicyclohexylammonium cations, when cations are involved through H bonding, dimerization of the tetrametallic component occurs leading to a hydrogen bonded cage structure. When $\text{OH}\cdots\text{Cl}$ intermolecular hydrogen bonds are considered a supramolecular architecture is obtained.

REFERENCES

1. Hathaway, B.J.: *Comprehensive Coordination Chemistry* (Editors: Wilkinson, G., Gillard, R.D., McCleverty, J.A.), 1st ed., volume 5, Chapter 53, Pergamon Press, Oxford, **1987**, 20-681;
2. Pouye, S.F., Cissé, I., Diop, L.: synthesis and infrared study of some new molybdate and hydrogenomolybdate adducts, derivatives and complexes of cadmium and antimony (V), *Scientific Study & Research - Chemistry & Chemical Engineering, Biotechnology, Food Industry*, **2009**, 10(4), 313-316;
3. Pouye, S.F., Cissé, I., Diop, L., Fall, D., Ciss, M.: Synthesis and infrared study of some new molybdate and hydrogenomolybdate adducts of SbF_3 , HgPh_2 and MX_2 ($\text{M} = \text{Cd}, \text{Hg}$; $\text{X} = \text{Cl}, \text{Br}$), *Scientific Study & Research - Chemistry & Chemical Engineering, Biotechnology, Food Industry*, **2012**, 13 (4), 43-48;
4. Cissé, I., Gueye, O., Diop, L.: Synthèse et caractérisation par spectroscopie infrarouge et Mössbauer de nouveaux composés molybdate de l'étain, *African Journal of Science and Technology*, **2003**, 10 (2), 90-94.