

SYNTHESIS AND INFRARED STUDY OF SOME HYDROGENOMOLYBDATO AND MOLYBDATO ADDUCTS OF SbF_3 , HgPh_2 AND MX_2 (M = Cd, Hg; X = Cl, Br)

Serigne Fallou Pouye¹, Ibrahima Cissé^{1*}, Libasse Diop¹,
Djibril Fall², Mounirou Ciss²

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

²Université Cheikh Anta Diop, Faculté de Médecine, de Pharmacie et
d'Odontostomatologie, Département de Pharmacie, Laboratoire de Chimie
Organique et Thérapeutique, Dakar, Sénégal

Corresponding author: icisse50@yahoo.fr

Received: January 5, 2011
Accepted: December 12, 2011

Abstract: Seven molybdato and hydrogenomolybdato new adducts with HgPh_2 , HgCl_2 , HgBr_2 , CdCl_2 , CdBr_2 and SbF_3 have been synthesized and characterized by infrared spectroscopy. The suggested structures are discrete, the oxyanions behaving as polychelating ligands. When non symmetrical cations are involved, supramolecular architectures are obtained.

Keywords: *coordinating molybdate, discrete structure, IR spectra*

INTRODUCTION

The coordinating ability of oxyanions has been reviewed by Hathaway [1] showing very scarce data on the molybdate anion. In the dynamic of our interest in the coordinating behavior of oxyanions, our group has yet published some papers dealing with [2-7]. In this paper, we have initiated the study of interactions between some molybdenic acid salts and HgPh_2 , MX_2 [$\text{M} = \text{Hg}, \text{Cd}$; $\text{X} = \text{Cl}, \text{Br}$] or SbF_3 , which has yielded seven new adducts, infrared study of which have been carried out and structures suggested on the basis of spectroscopic data.

EXPERIMENTAL

$(\text{Me}_4\text{N})_2\text{MoO}_4 \cdot \text{H}_2\text{O}$, $(\text{Cy}_2\text{NH}_2)_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, $(\text{CH}_6\text{N}_3)_2\text{MoO}_4 \cdot \text{H}_2\text{O}$ have been obtained as powders by complete or semi neutralization of H_2MoO_4 dissolved in hot water by a 20% water solution of Me_4NOH , Cy_2NH or guanidinium carbonate. When the salts are allowed to react with the metal halides in specific ratios, both as ethanolic solutions, precipitation occurs. The precipitates were stirred no less than two hours, filtered and left in the oven at 60°C .

The analytical data reported in Table 1 with the ratio salt/ MX_n have allowed suggesting the following formulae:

- C_1 : $(\text{Me}_4\text{N})_2\text{MoO}_4 \cdot 3\text{HgCl}_2$
 C_2 : $(\text{Me}_4\text{N})_2\text{MoO}_4 \cdot 4\text{HgCl}_2 \cdot 1/4(\text{Me}_4\text{NCl})$
 C_3 : $(\text{Me}_4\text{N})_2\text{MoO}_4 \cdot 4(\text{CdMoO}_4) \cdot 2\text{CdBr}_3 \cdot \text{Me}_4\text{N} \cdot 1/4(\text{Me}_4\text{NBr})$
 C_4 : $(\text{Cy}_2\text{NH}_2)_2\text{MoO}_4 \cdot 4\text{HgPh}_2 \cdot 1/12(\text{Cy}_2\text{NH}_2\text{OH})$
 C_5 : $(\text{Me}_4\text{N})_2\text{MoO}_4 \cdot 2\text{HgMoO}_4 \cdot \text{Me}_4\text{NBr}$
 C_6 : $\text{Sb}_2(\text{MoO}_4)_3 \cdot 1/6\text{Cy}_2\text{NH}_2\text{F}$;
 C_7 : $2(\text{CH}_6\text{N}_3\text{HMoO}_4) \cdot 3\text{SbF}_3$
 L_1 : $(\text{Me}_4\text{N})_2\text{MoO}_4 \cdot \text{H}_2\text{O}$
 L_2 : $(\text{Cy}_2\text{NH}_2)_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$
 L_3 : $(\text{CH}_6\text{N}_3)_2\text{MoO}_4 \cdot \text{H}_2\text{O}$

Table 1. Analytical data for $\text{C}_1 - \text{C}_7$

Compound	Ligand	Ratio (salt/ MX_n)	% calculated (% found)
C_1	L_1	1/4	C: 8.55 (8.45); H: 2.13 (2.16); N: 2.49 (2.48)
C_2	L_1	1/8	C: 7.60 (7.88); H: 1.90 (1.94); N: 2.21 (2.15)
C_3	L_1	1/2	C: 8.91 (8.86); H: 2.22 (2.30); N: 2.60 (2.70)
C_4	L_2	1/1	C: 44.33 (44.30); H: 4.72 (4.75); N: 1.40 (1.38)
C_5	L_1	1/3	C: 7.57 (7.37); H: 1.91 (1.91); N: 2.21 (2.18)
C_6	L_2	1/2	C: 3.16 (3.00); H: 0.53 (0.95); N: 0.31 (0.34)
C_7	L_3	1/2	C: 2.45 (2.42); H: 1.43 (1.49); N: 8.58 (8.67)

RESULTS AND DISCUSSION

IR main bands of the compounds C₁ – C₇ are presented in Table 2.

Table 2. IR main bands of the compounds C₁ – C₇

Compounds	Assignments			
	ν_1	ν_3	ν_2	ν_4
C ₁	-----	893 s	-----	448 m
C ₂	-----	880 s; 830 s; 800 s	-----	450 m
C ₃	925 m	879 m; 828 vs; 798 s; 730 s	435 m	384 m; 360 m; 353 m; 318 s
C ₄	-----	791.49 vs	-----	
C ₅	910 m	898 m; 877 m; 837 s; 788 s	457 w	419 m; 345 s; 322 w
C ₆	-----	805.44 vs; 850 br	-----	
C ₇	910 s	861 vs; 721 br		

br - broad; vs - very strong; s - strong; m - medium; w - weak; vw - very weak.

For C₁, the absence of ν_1 and the non splitting of ν_3 allow to conclude to Td symmetry for the molybdate anion. Then, we suggest a discrete structure with a trichelating anion with all the oxygen atoms involved in the coordination as shown in Figure 1.

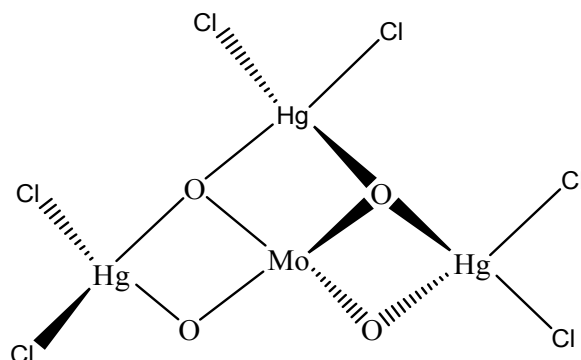


Figure 1. Proposed structure for C₁

For C₂, ν_1 is absent while ν_3 splits into several components because of crystal effects. According to the spectroscopic data, we suggest a discrete structure with a tetrachelating molybdate (Figure 2).

The appearance of ν_1 in compound C₃ is an indication of the presence of an anion of symmetry other than Td. The structure consists of two anions: [MoO₄(CdMoO₄)₄]²⁻ (containing a central tetrachelating anion with Td symmetry and monochelating molybdate anions) and [Cd₂Br₆]²⁻ with bridging Br⁻ (Figure 3).

The structure of C₄ is similar to the one of C₂. When the cations, through NH---O hydrogen bonds are involved, a supramolecular architecture is obtained (Figure 4).

For the compound C₅, the suggested structure is reported on Figure 5 with two types of MoO₄²⁻ anions: a bichelating central one and two monochelating external one.

The two the [MoO₄(HgMoO₄)₂]²⁻ are connected by bridging Br⁻. The appearance of ν_1 is consistent with this structure (Figure 5).

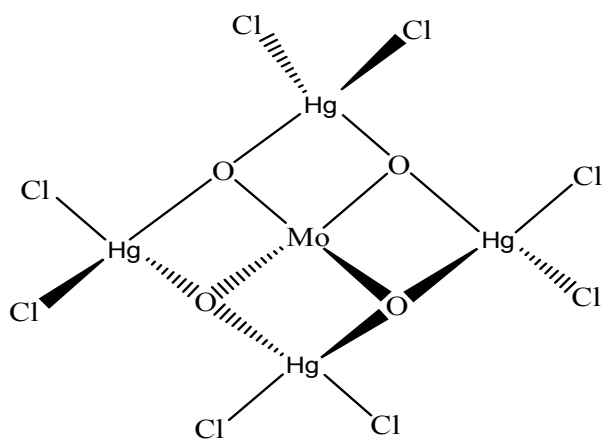


Figure 2. Proposed structure for C_2

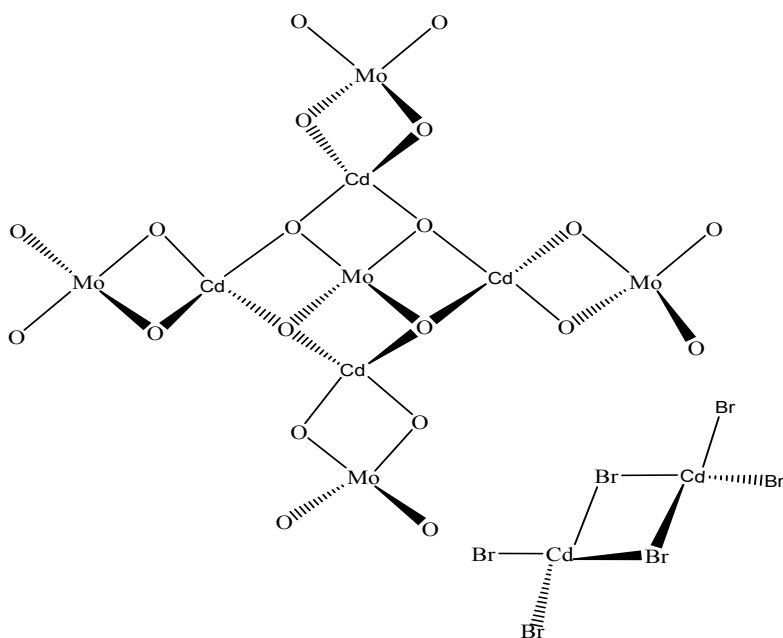


Figure 3. Proposed structure for C_3

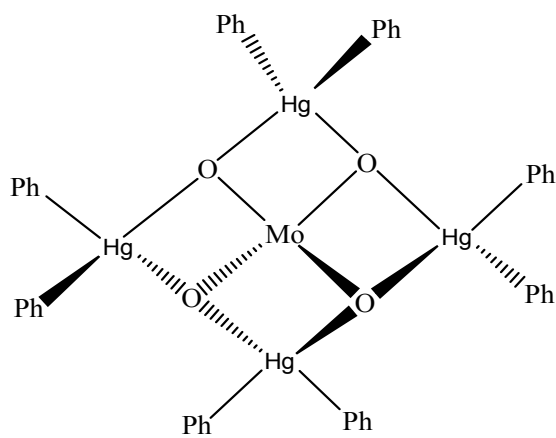


Figure 4. Proposed structure for C_4

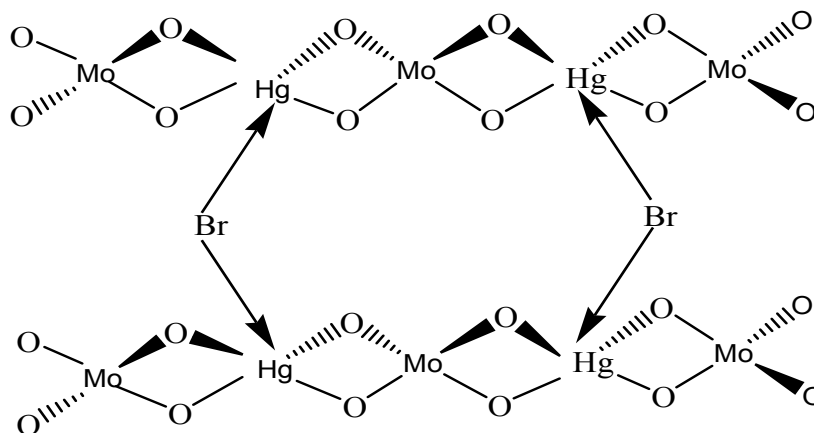


Figure 5. Proposed structure for C_5

The structure of C_6 is 3D as shown in Figure 6, with bichelating anions, the environment around Sb being octahedral.

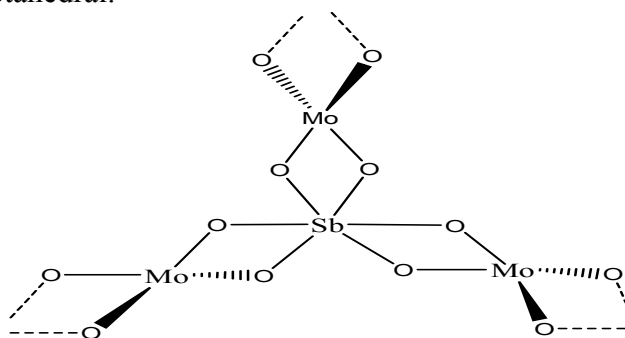


Figure 6. Proposed structure for C_6

C_7 can be considered as containing:

- 2SbF_4^- leading to the structure presented in Figure 7, or
- $[\text{Sb}_2\text{F}_9]^{3-}$ leading to the structure presented in Figure 8.

In both structures when cations are involved through $\text{N-H} \cdots \text{O}$ or $\text{N-H} \cdots \text{F}$ hydrogen bonds, supramolecular architectures are obtained.

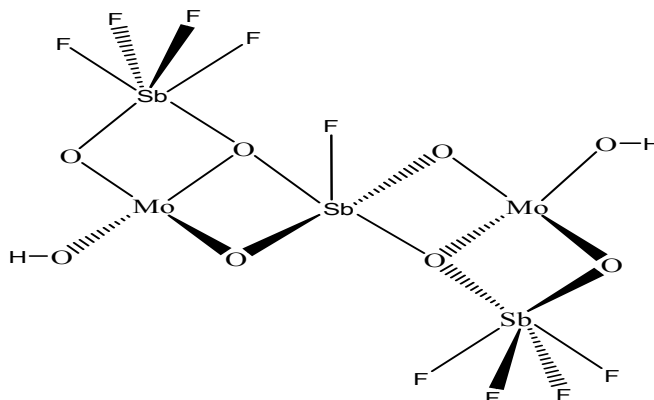


Figure 7. Proposed structure for C_7 with 2SbF_4^- anions

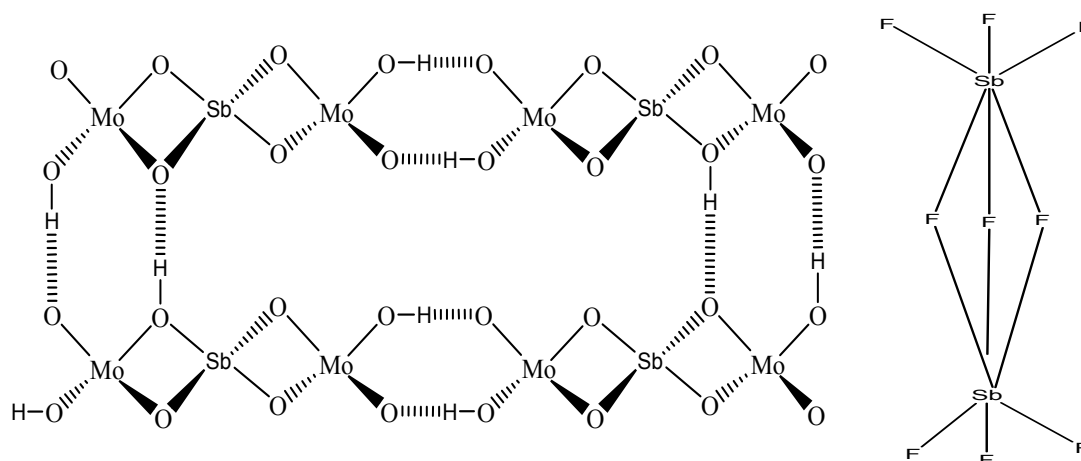


Figure 8. Proposed structure for C_7 with $[Sb_2F_9]^{3-}$

CONCLUSION

This work has allowed to obtain new molybdato and hydrogenomolybdato adducts and derivatives. The structures are discrete with bichelating, trichelating and tetrachelating molybdate anions. In the hydrogenomolybdato compounds, $HOMoO_3^-$ anion behaves as a monochelating or a bichelating ligand. When the non symmetrical cation $Cy_2NH_2^+$ is involved through hydrogen bonds, supramolecular architecture is obtained. The key role of the cation is noteworthy.

ACKNOWLEDGEMENTS

We thank Professor Tidiani, Cheikh Anta Diop University, Dakar, Senegal, for the equipment support.

REFERENCES

1. Hathaway, B.J.: *Comprehensive Coordination Chemistry*, 1st ed., Pergamon Press, **1987**, 413;
2. Diassé-Sarr, A., Diop, L., Mahon, M.F., Molloy, K.C.: *Main Group Met. Chem.*, **1997**, 20, 223;
3. Diop, C.A.K., Lahlou, M., Diop, L., Mahieu, B., Russo, U.: *Main Group Met. Chem.*, **1997**, 20, 681;
4. Sall, A.S., Diassé, A., Sarr, O., Diop, L.: *Main Group Met. Chem.*, **1992**, 15, 265;
5. Pouye, S.F., Cissé, I., Diop, L.: Synthesis and infrared study of some new molybdato and hydrogenomolybdato adducts, derivatives and complexes of cadmium and antimony (V), *Scientific Study & Research - Chemistry & Chemical Engineering, Biotechnology, Food Industry*, **2009**, 10 (4), 313;
6. Sarr, A.D., Cissé, I., De Barros, D.: *J. Soc. Ouest-Afric. Chim.*, **2004**, 017, 105;
7. Guèye, O., Qamar, H., Diop, L., Diop, C.A.: *Polyhedron*, **1993**, 12 (10), 1245;
8. Sall, A.S., Sarr, O., Diop, L.: *Bull. Chem. Soc. Ethiop.*, **1992**, 6 (1), 33.