

SYNTHESIS AND INFRARED STUDY OF SOME NEW MOLYBDATO AND HYDROGENOMOLYBDATO ADDUCTS, DERIVATIVES AND COMPLEXES OF CADMIUM AND ANTIMONY (V)

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Abstract: Five new molybdate adducts, derivative and complexes of Cd and Sb have been synthesized and studied by infrared. The structures are discrete, the anion behaving as a trichelating and polydentate ligand. The key role of Cy_2NH_2^+ in the supramolecular architecture is noteworthy.

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

INTRODUCTION

The coordination ability of oxyanions has been summarized by Hathaway [1]; Potier and al have reported some papers dealing with coordinating perchlorate containing compounds [2, 3]. Some molybdate complexes and derivative structures have yet been reported [4 – 6].

In our research work, we have been focusing on the coordination ability of oxyanions and have yet reported some paper dealing with [7]. We have carried out here the study of the interactions between $(\text{Me}_4\text{N})_2\text{MoO}_4 \cdot x\text{H}_2\text{O}$, $\text{Me}_4\text{NHMoO}_4$, $\text{Cy}_2\text{NH}_2\text{HMoO}_4$ and $\text{CdX}_2 \cdot n\text{H}_2\text{O}$ ($n = 1,4$) or SbCl_5 which has yielded five new molybdate and hydrogenomolybdate compounds, infrared study of which have been carried out and structures suggested on the basis of spectroscopic data.

EXPERIMENTAL

$\text{Me}_4\text{NHMoO}_4 \cdot t\text{H}_2\text{O}$, $(\text{Me}_4\text{N})_2\text{MoO}_4 \cdot x\text{H}_2\text{O}$, $\text{Cy}_2\text{NH}_2\text{HMoO}_4 \cdot y\text{H}_2\text{O}$ have been obtained as powders by totally or semi neutralizing H_2MoO_4 . When these salts as ethanolic solutions are allowed to react with $\text{CdCl}_2 \cdot \text{H}_2\text{O}$, $\text{CdBr}_2 \cdot 4\text{H}_2\text{O}$, SbF_3 or SbF_5 in specific ratio, precipitation occurs. The precipitates were stirred no less than two hours and washed with hot ethanol.

The analytical data reported in table 1 with the ratio salt/ MX_n ($\text{M} = \text{Cd}, \text{Sb}; \text{X} = \text{Cl}, \text{Br}$) has allowed to suggest the following formulae.

Table 1. Analytical data

Compounds	Ligand	Ratio (salt/ MX_n)	% cal (% found)
C ₁	L ₁	1/4	C : 10.97(10.95) ; H : 2.97(2.99) ; N : 2.99(3.00)
C ₂	L ₂	1/3	C : 14.43(14.44) ; H : 3.61(3.62) ; N : 1.40(1.50)
C ₃	L ₂	4/1	C : 16.23(16.15) ; H : 2.81(2.90) ; N : 1.57(1.65)
C ₄	L ₂	3/2	C : 14.90(15.08) ; H : 2.94(3.05) ; N : 1.45(1.45)
C ₅	L ₃	4/1	C : 12.06(11.90) ; H : 3.51(3.40) ; N : 3.51(3.44)
C ₆	L ₃	1/2	C : 0.81(0.76) ; H : 1.12(1.16) ; N : 0.23(0.26)

C₁: $(\text{Me}_4\text{N})_2\text{MoO}_4 \cdot 3\text{CdCl}_2 \cdot \text{H}_2\text{O}$

C₂: $(\text{Cy}_2\text{NH}_2\text{HMoO}_4) \cdot 3\text{CdCl}_2 \cdot 4\text{H}_2\text{O}$

C₃: $(\text{Cy}_2\text{NH}_2\text{HMoO}_4) \cdot 2\text{CdBr}_2$

C₄: $3(\text{Cy}_2\text{NH}_2\text{HMoO}_4) \cdot 2\text{Sb}(\text{HMoO}_4)_5$

C₅: $(\text{Me}_4\text{N})_3 \cdot \text{Cd}(\text{HMoO}_4)_5 \cdot 3\text{H}_2\text{O}$

C₆: $\text{Sb}(\text{HMoO}_4)_5 \cdot 1/6 \text{Me}_4\text{NCl} \cdot 2\text{H}_2\text{O}$

L₁: $(\text{Me}_4\text{N})_2\text{MoO}_4 \cdot \text{H}_2\text{O}$

L₂: $(\text{Cy}_2\text{NH}_2\text{HMoO}_4) \cdot 4\text{H}_2\text{O}$

L₃: $(\text{Me}_4\text{N})\text{HMoO}_4 \cdot 2\text{H}_2\text{O}$

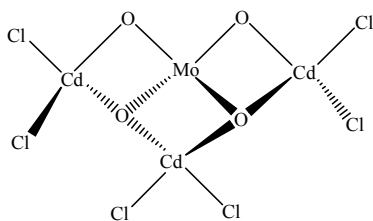
RESULTS AND DISCUSSION

The infrared data of the title new compounds have been reported in tables 1 and 2.

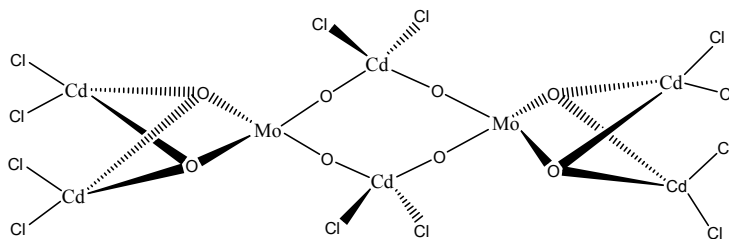
The group theory works well when the oxyanions are neutral and non substituted; in these cases the number of bands allows easily to deduce the symmetry of the anion and the mode of coordination.

In the case of C₁, the nonsplitting of $\nu_3\text{MoO}_4$ and the absence of $\nu_1\text{MoO}_4$ allow to conclude to the presence of MoO_4^{2-} belonging to Td symmetry group. On assuring a tetrahedral environment for the Cd centre we suggest a discrete structure with a trichelating molybdate (Schemes 1a and 1b).

In the cases of five hydrogenomolybdate adducts and derivative, while not being able to correlate the number of bands and the type of coordination, we suggest the following structures when not involving the cation (schemes 2a and 2b). The structures are built upon the acid acetic type hydrogen bonded dimer $-(\text{MO}_4\text{H})_2---$



Scheme 1a

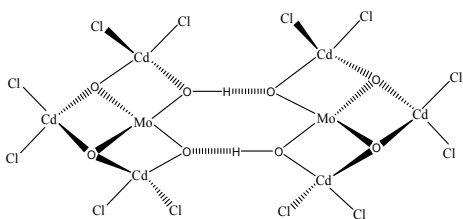


Scheme 1b

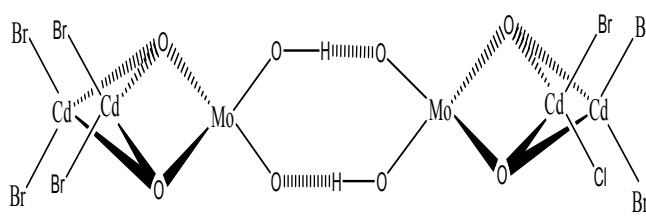
Table 2. IR bands fundamental of the compounds C2....C6

Vibrations Compounds	νMoO_4	δMoO_4	$\nu\text{N-H}$	$\nu\text{OH}, \nu\text{NH}_2; \delta\text{NH}_2$
C ₁	787 vs	-----	-----	-----
C ₂	810m ; 778m	670m ; 582 ; 554w	2939 ; 2859s	3036 ; 3546 ; 3632br
C ₃	913 ; 660 ; 897 ; 799 ; 787	557 ; 481w	2937 ; 2858s	3475br
C ₄	955s ; 913s ; 813s ; 660s	-----	2936 ; 2870s	3246 ; 3429br
C ₅	905s ; 885s ; 660sh	556 ; 402vw	-----	3250 ; 1760br
C ₆	957s ; 890s ; 881s ; 851s	-----	2961 ; 2912s	3391 ; 3019 ; 3012 ; 1632

vs: very strong ; s: Strong; w: weak ; vw: weak; m: medium; br: broad

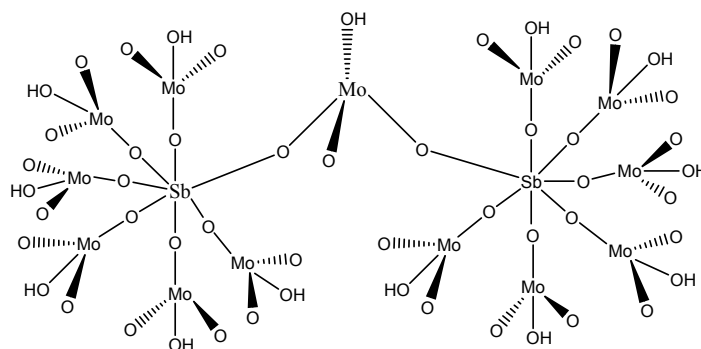


Scheme 2a



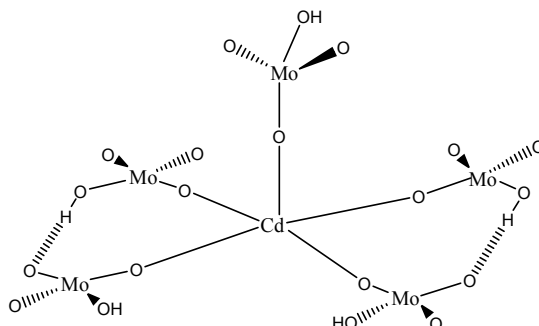
Scheme 2b

(The size of the bromine has surely not allowed coordinating three molecules of CdBr_2 as in 2a).



Steric effects have not allowed fixing a third molecule of $\text{Sb}(\text{MoO}_4\text{H})_6\text{NMe}_4$ to the central HOMoO_3 - the coordination number of 7 for Sb is very common as in [8 – 11].

For C_5 or C_6 the suggested structures are discrete with a square pyramid environment around the Cd centre or a trigonal bipyramid as in $CdCl_5^{3-}$ or $SbCl_5$.



C_5 , C_6 are obtained from a substitution of the chloride ions of $(CdCl_5)^{3-}$ or $SbCl_5$ by MoO_4H . On involving the cation while considering C_2 , C_3 , C_4 , supramolecular architectures are obtained.

CONCLUSION

The six molybdate (one) and hydrogenomolybdate (five) adducts, and derivative studied here, have discrete structures, the neutral molybdate behaving as a polychelating ligand or monodentate. When the cation is involved supramolecular architectures are obtained.

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