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SYNTHESIS AND INFRARED STUDY OF SOME NEW SULPHATO AND TUNGSTATO DERIVATIVES AND ADDUCTS OF CADMIUM, ZINC AND MERCURY DIHALIDES

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Résumé : Dix complexes et dérivés sulfato et tungstato d'halogénures du cadmium, du zinc et du mercure ont été synthétisés et des structures proposées sur la base de leurs données infrarouge. Le sulfate et le tungstate se comportent dans tous ces composés comme polychélatants avec quelques monocoordinations suplémentaires dans certains cas.

Keywords: Polynuclear adducts - Infrared data - Discrete structure - C_{3v}, C_{2v} and Td symmetry sulphate or tungstate-

I - INTRODUCTION

The behaviour of oxyanions as ligands has been reviewed by Hathaway(1).

In the framework of our research work for understanding the behaviour of the tetrahedral oxyanions acting as ligands some papers have been reported from our laboratory (2-7).

The aim of this work is to synthesize new polynuclear sulphato and tungstato adducts and derivatives and suggest structures on the basis of their i.r.data, to deduce the type of coordination in which the oxyanions are involved. At the opposite of tin derivatives, mercury, cadmium and zinc derivatives are not detectable by Mössbauer studies (iron and tin atoms are the most suitable for Mössbauer studies)

II - EXPERIMENTAL

All the compounds were obtained as white precipitates on mixing both ethanolic solutions of MX_2 or a mixture of MX_2 and $M'X_2$ (M or M'= Zn, Cd, Hg; X=Cl, Br) with the quaternary ammonium such as

$(Me_4N)_2SO_4.2H_2O$, $(Et_4N)_2SO_4$ $4.5H_2O$ and $Me_4NHWO_4.2H_2O$ in defined ratio (these salts were obtained as white powders after a slow evaporation of a water solution mixture of tetralkylammonium hydroxyde and H_2SO_4 -98% - or H_2WO_4 -97%- in neutralizing amounts). The precipitates were stirred during more than two hours, filtered and washed with hot ethanol.

The elemental analyses performed by the "Service Central d'Analyses" C.N.R.S. Vernaison, France are reported in Table I with the metal to ligand ratio.

A = $(Me_4N)_2SO_4.3CdBr_2$

B = $(Me_4N)_2WO_4.2HgWO_4$

C = $(Et_4N)_2SO_4.2ZnSO_4.H_2O$

D = $(Me_4N)_2WO_4.2CdWO_4$

E = $3(Me_4N)_2SO_4.CdSO_4.4CdBr_2$

F = $3(Me_4N)_2WO_4.HgWO_4.4HgCl_2$

G = $(Et_4N)_2SO_4.2Hg_2Cl_5NEt_4.2ZnCl_2$

H = $2(Et_4N)_2SO_4$ $3HgCl_2.2ZnCl_2$

I = $2(Me_4N)_2WO_4.5HgCl_2$

J = $(Et_4N)_2SO_4.ZnCl_2.3HgCl_2$

	Ratio metal to ligan	% C	% H	% N	% X	% M
A	1 - 4	9.04(9.34)	2.26(2.24)	2.63(2.63)	45.29(44.82)	31.77(31.00)
B	2 - 1	7.18(6.87)	1.79(1.93)	2.09(1.79)	-	30.00(30.80)
C	2 - 1	27.55(27.09)	6.02(6.87)	4.01(4.09)	-	18.29(19.02)
D	2 - 1	8.59(7.72)	2.15(2.44)	2.50(1.95)	-	20.13(20.89)
E	2 - 1	14.18(13.90)	3.54(4.12)	4.13((3.92)	31.50(31.45)	27.68(27.44)
F	2.5 - 1	10.58(10.03)	2.64(2.67)	2.03(2.73)	10.43(9.67)	36.83(35.82)
G	1(2 - 2)	18.77(18.40)	3.91(3.88)	2.73(2.59)	24.20(23.86)	%HG 39.20(39.73) %ZN 6.39(5.76)
H	1(3 - 1)	21.34(21.20)	4.44(4.38)	3.11(2.93)	19.73(19.34)	%HG 33.43(32.97) %ZN 7.26(7.59)
I	1 - 4	8.95(8.89)	2.23(2.11)	2.90(2.40)	16.51(15.37)	46.64(45.20)
J	1(- 3)	14.69(14.26)	3.06(3.34)	2.14(2.20)	21.73(21.34)	%HG 46.02(45.9) %ZN 5.00(4.88)

%Calculated (%Found)

Tableau 1 : *In mixed metal chlorides containing compounds the numbers in parentheses indicate the ratio $ZnCl_2/HgCl_2$*

The i.r. spectra were scanned on a Perkin Elmer 180 spectrometer as nujol mulls (4000-200cm^{-1}) or F.T.I.R Nicolet 5300 (600-50cm^{-1}) using CsI or polyethylene windows.

III - RESULTS AND DISCUSSION

III.1 General considerations

A non substitutued tetrahedral oxyanion of AO_4^{n-} type has four vibrations according to the 3n-6 vibrations rule for non linear molecules : two of F_2 type triply degenerate (ν_3 the antisymmetrical stretching vibration and ν_4 the antisymmetrical bending vibration), one of

A_1 type non degenerate (ν_1 the symmetrical stretching vibration) and one of E type doubly degenerate (ν_2 the symmetrical bending vibration).

- When the anion has Td symmetry ν_1 is absent (it is only in this symmetry that ν_1 is absent), ν_3 and ν_4 do not split
- when the anion is monocoordinated (C_{3v} symmetry) ν_3 splits into two bands (A_1 + E) and ν_1 allowed by the symmetry rule, appears.
- When the anion is symmetrically bicoordinated ν_3 splits into three bands and ν_1 appears too.

So the absence of ν_1 or the number of bands of ν_3 and ν_4 the appearance of n_1 are a reliable criterion to deduce the point group of the oxyanions and the coordination way. (The Raman data is so no necessary). The frequencies of the vibrations of the main oxyanions are reported in (8).

III - 2 Infrared study and suggested structures

The I.R. data of title adducts and derivatives are reported on Table II with the symmetry of the oxyanion (the cations bands are arbitrary omitted).

The following structures of the MX_2 adducts are suggested mainly assuming a tetrahedral environment around the metallic centers as in $(Et_4N)_2SO_4.2CdX_2$(**5**) which contains a Td symmetry sulphate. No spectroscopic method allows to determine the environment of these metallic centers. At the opposite of tin compounds, which Mössbauer data allow to determine the environment.

On the i.r.spectrum of the adduct A, the presence of ν_1 at 995cm^{-1} and the splitting of ν_3 into two bands are consistent with a sulphate of C_{3v} symmetry (8) : a discrete structure with trichelatant sulphate involving only three of the oxygens is suggested (Figure 1).

The multiplicity of the bands in the region of ν_3 and ν_4 (four bands) and the presence of ν_1 at 925 cm^{-1} allow to consider two types of tungstate in the derivative B (one with Td symmetry and two with C2v Symmetry). So, a discrete structure with central bichelatant tungstate and two chelatant terminal ones is suggested with tetrahedral environment around the mercury centers (Figure 2)

	ν_3	ν_1	ν_4	ν_2	$\nu M-O$	$\nu M-X$	Sym $AO_4^=$
A	1178 vs 1086 s	995 sh	589 m 553 m	275 m	200 m	150 s	C3v
B	880 s 840 s 800 s 680 s	925 m	490 m 430 sh 410 m 370 s	580 m	244 m	-	C2v + Td
C	1118 vs	-	617 m	-	261 s	-	Td
D	830 vs	920 sh	380 m	600 tr	230 sh	-	Td
E	1093 vs	978 tr	603 m	451 sh	224 sh	178 vs	Td
F	860 sh 820 vs	925 sh	418 w 400 sh 375 w	-	255 sh	225 m	Td
G	1111vs	-	617 m	437 tr	Zn-O - Hg-O 288m	Zn-Cl 278 m Hg-Cl 251m	Td
H	1113 vs	980 tr	615 m	450 tr	Zn-O 264 sh Hg-O 288 m	Zn-Cl 277 m Hg-Cl 251m	Td
I	820 vs	-	365 sh	-	275 sh	260 m	Td
J	1109 vs	-	617 m	450 tr	Zn-O 309 m Hg-O 294 sh	Zn-Cl 277 m Hg-Cl 251 m 245 m	Td

vs = very strong *s= strong* *m = medium*
sh = shoulder *w = weak* *tr= trace*

Tableau II : *The I.R data of litle adducts and derivatives*

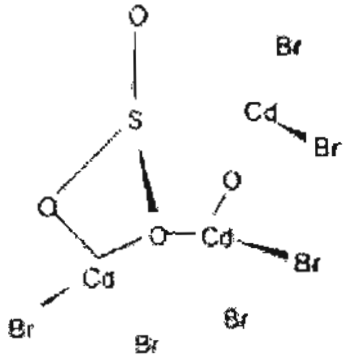

Figure 1

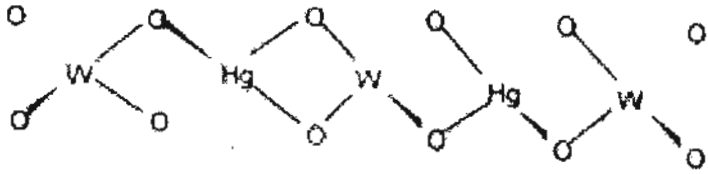

Figure 2

The absence of ν_1 and ν_2 or their appearance as trace indicates Td symmetry for the oxyanions in all the other derivatives (C to J).

A tridimensional structure with bichelatant oxyanions is suggested for the adducts C and D, the environment of the metal being octahedral (Figure 3)[any other structure would give another symmetry for the oxyanion] ; the existence of an octahedral environment of zinc and cadmium has been reported in the solid state in $(Zn(NH_3)_6)^{2+}$(9) and $(Cd(NH_3)_6)^{2+}$) (10)

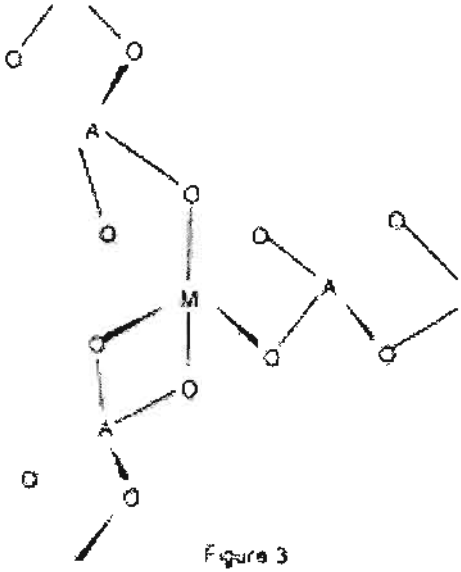

Figure 3

M = Zn,Cd , A = S, W

The suggested structure of the adducts E and F keeping the oxyanion in a Td symmetry is discrete with an octacoordinated cadmium or mercury (Figure 4) ; the coordinated oxygens four by four belonging to the same plane[any other structure would not respect the symmetry constraints]. This exceptional coordination number for the cadmium has been reported in catena-bis(m-6-amino-3 methyl-5 nitroso-uracile N^5,O^4,N^1,O^1) cadmium (II) (11) and in the complex anion $(Hg(NO_2)_4)^{2-}$(9) in which the nitrite acts as a monochelating ligand.

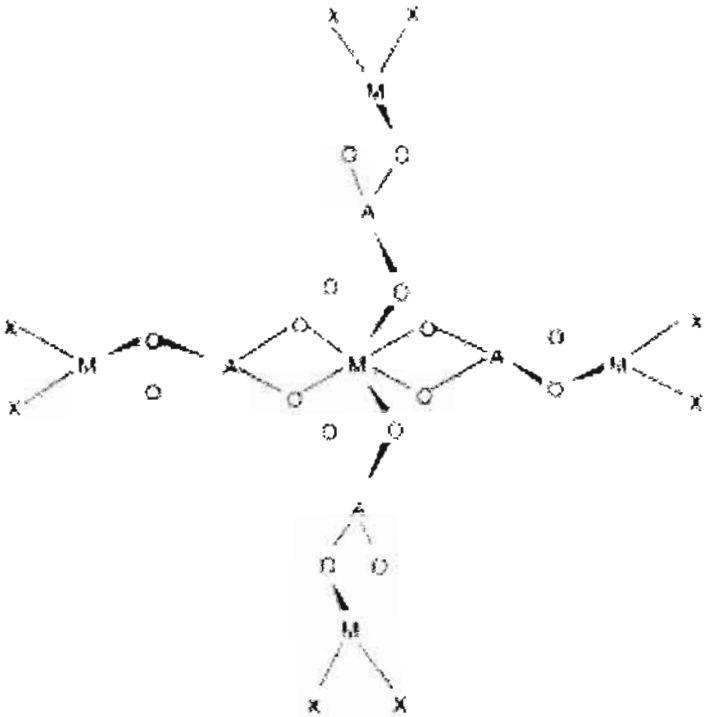

Figure 4

M=Cd Hg X=Br,Cl

A discrete structure is suggested for the adduct G with bichelatant and tetra-unidentate sulphate (Figure 5).This structure is similar to the structure reported for $(Et_4N)_2SO_4.6HgCl_2.2H_2O$ (5), (notice that the formula of the adduct G can be deduced from $(Et_4N)_2SO_4.6HgCl_2.2H_2O$ on substituting two $HgCl_2$ molecules by two $ZnCl_2$ molecules and the two water molecules by two chlorides), the chlorides as the water molecules bridging the $HgCl_2$ molecules .

The adducts H and I can be considered as a 1 : 2 adduct of $HgCl_2$ and $(R_4N)_2AO_4.2MCl_2$ (R=Me,Et ; A=S,W ; M=Hg,Zn) (these last adducts

have yet been reported and contain a Td symmetry sulphate (5));

The oxyanion having Td Symmetry in H and I, we can reasonnably suggest a structure in which two adducts $(R_4N)_2AO_4.2MCl_2$ are sandwiching one $HgCl_2$ molecule (Figure 6); the interactions between $(R_4N)_2AO_4.2MCl_2$ adducts and $HgCl_2$ do not prevent the oxyanion from having a Td symmetry because all the oxygens are involved in bonding and the oxyanion appears "roughly" as having a Td symmetry (the degrees of perturbation of the oxygens are not enough different to be detectable by infrared spectroscopy)

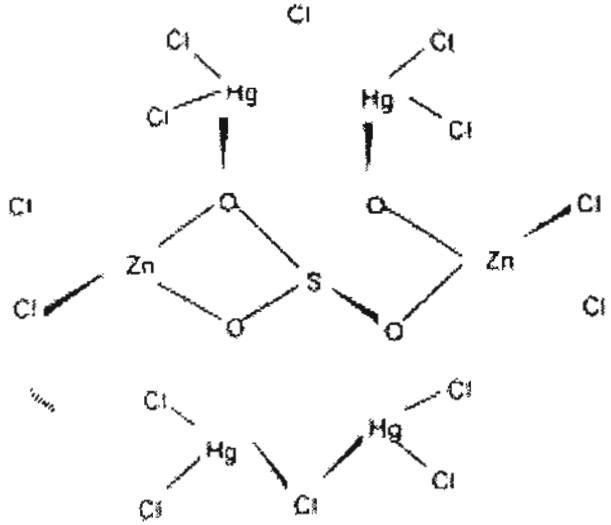

Figure 5

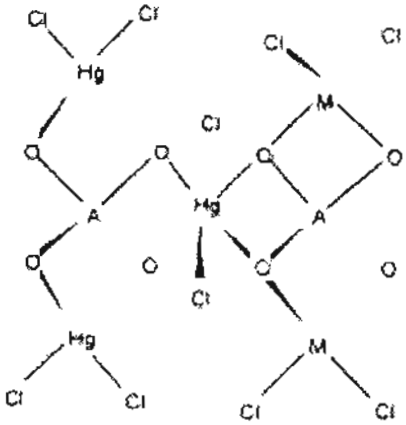

Figure 6

M=Hg, Zn, A = S, Vx

The structure of J is discrete with a tetrachelating sulphate (Figure 7); the difference of perturbation of the oxygens linked to different metallic centers is too small to prevent the sulphate from appearing in the i.r. spectrum with a Td symmetry.

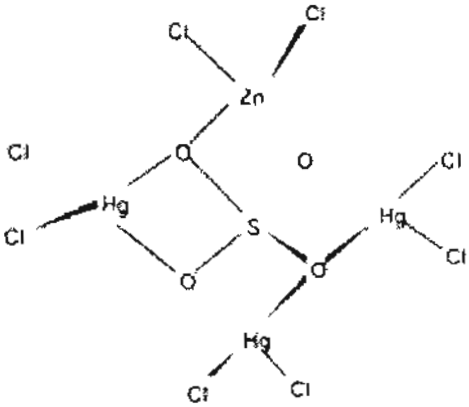

Figure 7

IV - CONCLUSION

The sulphate and the tungstate behave in these adducts as a bi, tri or tetrachelatant ligand with or without unidentate extra coordinations and involves discrete structures.

In the pentanuclear adduct $3(Me_4N)_2AO_4.MAO_4.4MX_2$ the octa-coordinated cadmium and mercury are noteworthy.

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