

Synthesis And Infrared Study Of New Tungstato Polynuclear Cadmium (ii) And Mercury (ii) Complexes

Synthèse et étude infrarouge de nouveaux complexes tungstato polynucléaires du cadmium (ii) et du mercure (imi)

DE BARROS Dinora¹, DIALLO Waly¹ And DIOP Libasse^{1*}

Abstract :

Eleven new polynuclear tungstato $MX_2(X=Cl, Br)$ adducts were synthesized and studied by infrared spectroscopy. The suggested structures are discrete, the tungstate anion behaving as a bi-, tri- and tetrachelating ligand.

Résumé :

Onze nouveaux complexes tungstato polynucléaires ont été synthétisés et étudiés par spectroscopie infrarouge. Les structures proposées sont discrètes, l'ion tungstate se comportant comme un ligand bi-, tri- et tétrachélatant.

Mots clés :

Complexes tungstato polynucléaires, anion tungstate, structure discrète, infrarouge, ligand bichélatant trichélatant, tétrachélatant.

Key words :

Polynuclear tungstato adducts, tungstate anion, infrared, discrete structures, bichelatant, trichelatant, tetrachelatant ligand.

^{1*} **Correspondant : Libasse DIOP**, Laboratoire de Chimie Minérale et Analytique (LACHIMIA).
Département de Chimie, Faculté des Sciences et Techniques,
Université Cheikh Anta Diop, Dakar, Sénégal

1 - Introduction

The main results on the coordination chemistry of oxyanions have been reviewed by Hathaway [1]. The coordinating behaviour of the perchlorate anion has been studied by Pascal and coll [2-4]. The coordinating behaviour polytungstate anions has been studied [5-7], some results have also been obtained on tungstato complexes [8, 9].

Since many years our laboratory has been involved in research dealing with the coordinating ability of tetrahedral and pyramidal oxyanions [10-13].

In the aim of getting more informations on the behaviour of tungstate ions (WO_4^{2-} and HWO_4^-), we have initiated the study of the interactions between salts such as $(\text{Me}_4\text{N})_2\text{WO}_4 \cdot \text{Me}_4\text{NHWO}_4 \cdot 2\text{H}_2\text{O}$ or $(\text{Et}_4\text{N})_2\text{WO}_4 \cdot \text{Et}_4\text{NHWO}_4 \cdot 4\text{H}_2\text{O}$ and the dihalides of Cd and Hg. The adducts obtained have been studied by infrared spectroscopy and structures suggested on the basis of the infrared data.

2. - Experimentals

2.1 - Synthesis Of The Tungstic Acid Salts
 $(\text{Me}_4\text{N})_2\text{WO}_4 \cdot \text{Me}_4\text{NHWO}_4 \cdot 2\text{H}_2\text{O}$ (L_1) and $(\text{Et}_4\text{N})_2\text{WO}_4 \cdot \text{Et}_4\text{NHWO}_4 \cdot 4\text{H}_2\text{O}$ (L_2) were prepared by mixing water solutions of the appropriate tetraalkylammonium hydroxyde (MERCK) with tungstic acid H_2WO_4 97 % (MERCK). The white powder obtained after solvent evaporation, is recrystallized from EtOH, washed with éther and kept under P_2O_5 .

2.2 - Synthesis Of Complexes

All the compounds were obtained as white precipitates on mixing both ethanolic solutions of MX_2 ($M = \text{Cd}, \text{Hg}$; $X = \text{Cl}, \text{Br}$) with the quarternary ammonium salt (L_1) and (L_2) in defined ratio (ligand/ MX_2). The precipitates were non stirred or stirred during more than two hours, filtered and washed with hot ethanol.

The analytical data are reported in table I. Elemental analyses were performed by the Analytical Laboratory of the Department of Inorganic and Analytical Chemistry (University of Padova, Italy) and the CNRS « Service Central d'Analyses », Vernaison, France.

The infrared. Spectra were scanned on a 580 Perkin-Elmer spectrometer as nujol mulls ($4000\text{-}200\text{ cm}^{-1}$) or a Bruker FTIR ($600\text{-}50\text{ cm}^{-1}$) spectrometer using CsI or polyethylene plates.

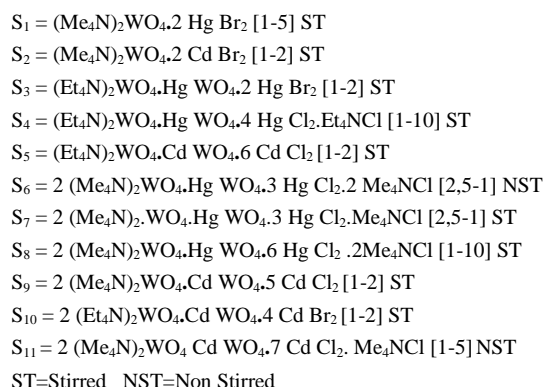


Table I : Elemental data of the complexes

Adducts	% C	% H	% N	% X	% M
S ₁	8,59 (8,06)	2,14 (2,10)	2,50 (2,16)	-	35,90 (35,10)
S ₂	10,21 (9,20)	2,55 (2,28)	2,98 (2,67)	33,99 (33,54)	23,90 (24,91)
S ₃	11,44 (11,68)	2,38 (2,31)	1,66 (1,88)	-	35,88 (35,10)
S ₄	13,04 (13,37)	2,71 (2,77)	2,05 (1,89)	14,48 (13,38)	45,39 (44,86)
S ₅	15,51 (14,46)	3,23 (3,23)	2,26 (2,61)	17,18 (16,12)	31,78 (30,12)
S ₆	12,19 (12,29)	3,04 (3,27)	3,56 (3,34)	12,02 (12,94)	33,96(31,48)
S ₇	10,09 (10,03)	2,52 (2,67)	2,94 (2,73)	10,44 (9,67)	33,74(32,82)
S ₈	9,32 (8,89)	2,33 (2,11)	2,72 (2,40)	16,07 (15,37)	45,46 (44,25)
S ₉	9,28 (8,91)	2,32 (2,36)	2,70 (2,71)	17,16 (17,82)	32,59(32,07)
S ₁₀	15,57 (14,63)	3,24 (3,14)	2,27 (2,21)	29,21 (27,76)	24,64(23,09)
S ₁₁	9,43(9,52)	2,35(2,42)	2,75(2,67)	20,89(21,40)	-

% calculated (% found)

3. - Results And Discussion

The infrared data of the adducts are presented in table II with the assignments based on literature data [8]

A - (Me₄N)₂WO₄·2 MBr₂(M=Hg, Cd) (S₁ and S₂)

The absence of ν_2 (symmetrical bending mode) is an indication of Td symmetry for the tungstate ion according to Group Theory. The intense envelope of ν_3 (antisymmetrical stretching mode) with many components (due to crystal effects) is consistent with Td symmetry for the tungstate ion. The suggested structure for S₁

is a discrete one with a bichelating tungstate anion, the environment around the mercury atom being tetrahedral (**figure I**). In the bichelation all the oxygen atoms are involved.

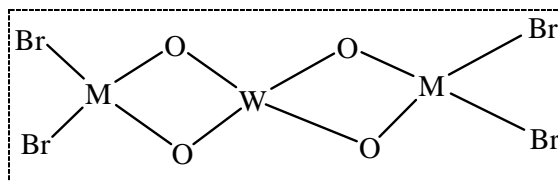


Fig I

The splitting of ν_4 into three bands ($2A' + A''$) and the appearance of ν_2 as two bands

Table II : Infrared data of the adducts

Attribution→ Adducts ↓	ν_1 WO ₄	ν_3 WO ₄	ν_2 WO ₄	ν_4 WO ₄	ν_{M-O}	ν_{M-X}
S ₁	920 tr	870 sh 800 s 680 sh	--	405 sh 370 w	--	187 s
S ₂	920 m	875 w 805 shs 750 ep 650 s	575 m	503 w 405 m 315 m	260 m	178 s
S ₃	930 vs	815 s 780 s 740 sh	533 sh	420 s,d 414 360 m	210 w	192 s
S ₅	920 w	875 w 810 s 650 w	570 m	505 w 405 m 305 m	240 s	260 sh
S ₄	930 tr	810 } 800 } <i>doublet</i>	583 w	445 s	250 sh	240 s
S ₆	925 w	820 s 780 sh	--	400 s	255 sh	225 s
S ₇	925 tr	860 sh 820 - 780 (W.A.)	--	410 sh 400 m 375 sh 365 m	255 sh	225 s
S ₈	930 tr	820 s	--	360 w	275 sh	260 m
S ₉	920 m	875 w 810 s 650 s	575 m	505 m 405 m 315 m	255 m	200 m
S ₁₀	920 tr	850 - 645 (W.A.)		500 w 405 w 310 w	255 w	300 w
S ₁₁	920 tr	850 vs	580 s	500 m 405 w	350s	299s

vs = very strong; s = strong; m = medium; sh = shoulder; w = weak; tr = trace.; W.A.=wide absorption

($A' + A''$) on the infrared spectrum of S_2 are consistent with a tungstate ion in C_s symmetry. The suggested structure for S_2 is discrete with a tri-oxygen atoms bichelating tungstate anion (**figure II**).

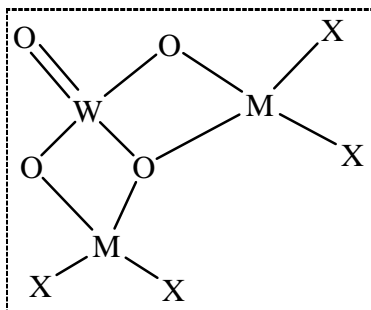


Fig II



Considering the spectrum of S_3 , the non splitting of ν_3 and ν_4 is a indication of Td symmetry for the tungstate anions. The suggested structure for these complexes is discrete with a central metal cation bichelated by two tungstate anions linked to one molecule of $HgBr_2$ (**figure III**), the environment around the metal being tetrahedral as predicted by the Ligand Field Theory when extra ligand addition does not occur.

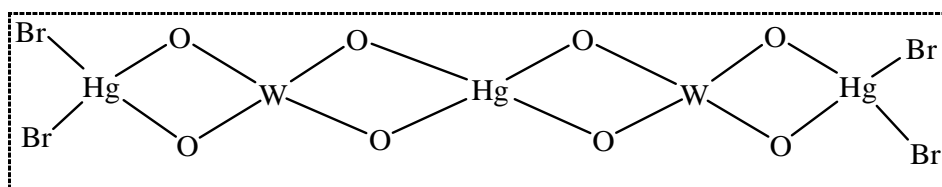


Fig III : **C** – $(Et_4N)_2WO_4 \cdot MWO_4 \cdot nMCl_2 \cdot mEt_4NCl$ ($M=Cd, Hg$) ($n=4, 6$; $m=0, 1$) (S_4, S_5)

The non splitting of ν_4 on the spectrum of S_4 indicates Td symmetry for the tungstate anion and allows to consider S_4 as a central M^{2+} cation chelated by two $[WO_4(MX_2)_2]^{2-}$ complex-anions (**figure IVa**); the additional chloride ion can be linked to the central Hg^{2+} , the environment around the metal being tetrahedral.

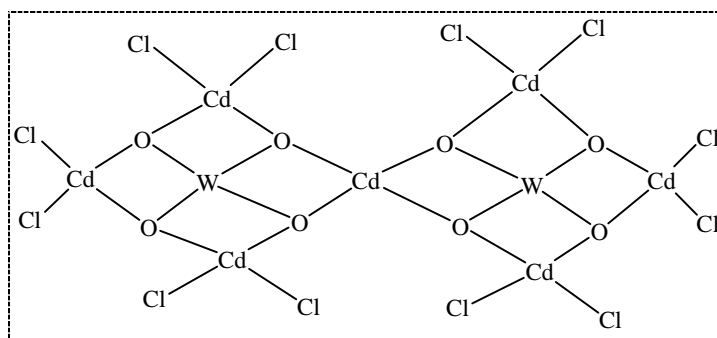


Fig IVb

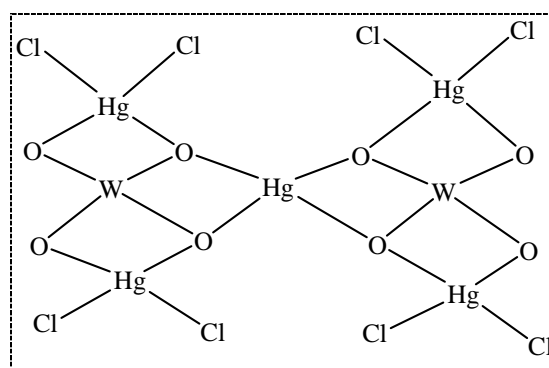
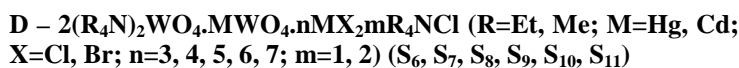


Fig IVa

In the case of S_5 , the two complex-anions chelating the central metal are $[WO_4(MX_2)_3]^{2-}$ (**figure IVb**).

The appearance of ν_1 as a trace or weak on the infraed spectra allows to consider Td symmetry for the tungstate ion. These complexes can be considered as a central M^{2+} ion surrounded by three $[WO_4 \cdot HgCl_2]^{2-}$ in S_6 and S_7 , two $[WO_4 \cdot (CdCl_2)_2]^{2-}$ and one $[WO_4 \cdot CdCl_2]^{2-}$ in S_9 , one $[WO_4 \cdot (CdBr_2)_2]^{2-}$ and two $[WO_4 \cdot (CdBr_2)]^{2-}$ in S_{10} , three $[WO_4 \cdot (HgCl_2)_2]^{2-}$ in S_8 , one $[WO_4 \cdot (CdCl_2)_3]^{2-}$ and two $[WO_4 \cdot (CdCl_2)_2]^{2-}$ in S_{11} ; the additional chloride ions are linked to the central metallic cation involving a eight S_6 , S_8 or seven S_{11}

coordinated cadmium or mercury witch coordination sphere are wide enough.

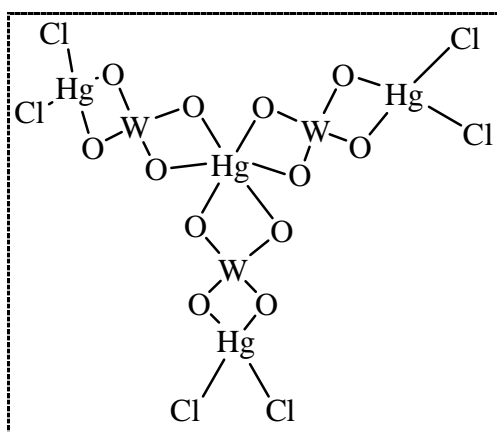


Fig.V (S₆, S₇)

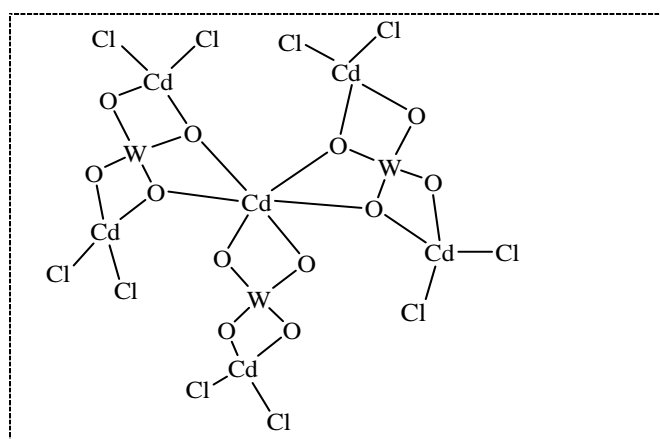


Fig.VI (S₉)

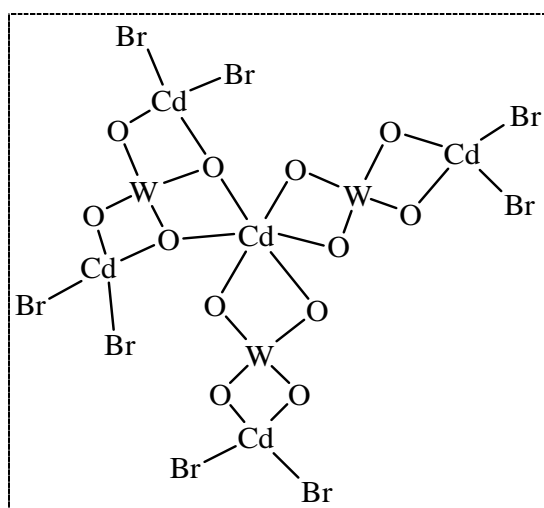


Fig.VII (S₁₀)

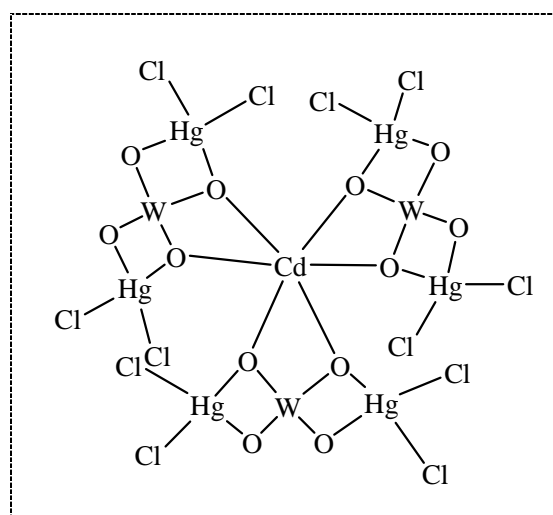


Fig.VIII (S₈)

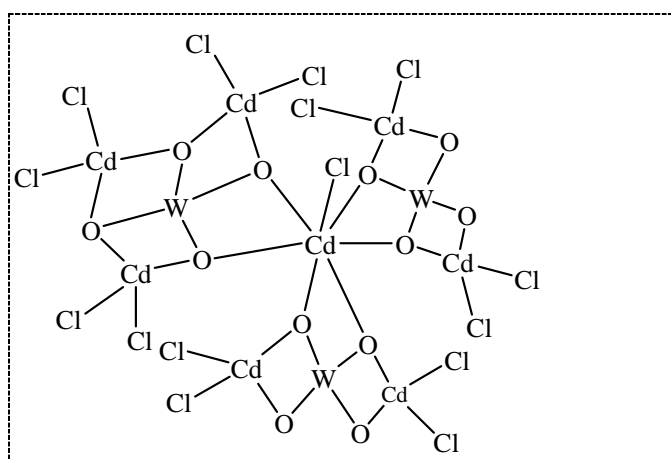


Fig.IX (S₁₁)

4 - Conclusion

The dinuclear tungstato complexes contain one bichelating tungstate anion involving three or four oxygen atoms, the trinuclear complex two bichelating tungstate anions, the tetranuclear complexes three bichelating tungstate anions, the pentanuclear complex, one trichelating and two bichelating anions, the hexanuclear complex two trichelating and one bichelating tungstate, the heptanuclear complex, three trichelating tungstate anions. Extra addition of chloride ions on the central metal occurs in some complexes.

5- Acknowledgements

Mrs D. De B. thanks Professor M. Vidali (University of Padova - Italy) for equipment support and providing some elemental analysis.

6- References

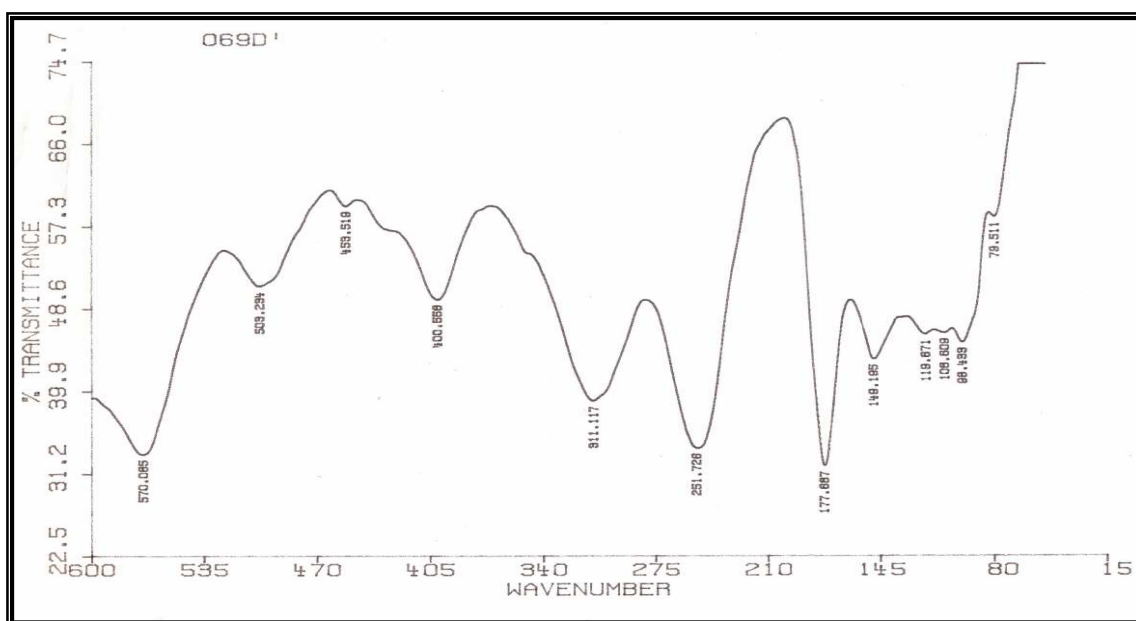
- [1] Hathaway B. J., « Comprehensive Coordination Chemistry », Vol 2, Pergamon Press (1987) 413.
- [2] Pascal J. L. and Potier J., *Courrier du C.N.R.S., Images Chim.*, (1985) 60, 14.
- [3] Pascal J. L. and Potier J., Zhang C. S., *J. Chem. Soc. Dalton Trans* (1985) 297.
- [4] Pascal J. L. and Favier F. *Coordination Chemistry Reviews*, 209(2000) 453 – 457.
- [5] Knaust J. M., Inman C. and Keller S. W., *Chem. Commun.* (2004), 492.
- [6] Wang J. P., Guo D. J. and Niu J. Y., *Chin. J. Inorg. Chem.*, (2003), 19, 579.
- [7] Reinoso S., Victoria P., Gutierrez-Zorrilla J. M., Lezama L., Felices L. S. and Beitia J. L., *Inorg. Chem.*, (2005), 44, 9731.
- [8] Dequeant M. Q., Mc Guire R. Jr, McMillin D. and Ren T., *Inorg. Chem.*, (2005), 44, 6521
- [9] Chio K. Y., Park L. H. J. R., Kim Y. J. and Ryu H., *J. Korean Chem. Soc.*, (1998), 42, 9731.
- [10] Sarr O. and Diop L., *Spectrochim Acta*, 46A, 8, (1990) 1239.
- [11] Sall A. S. and Diop L., *Inorg. Chim. Acta*, 171 (1990) 53.
- [12] De Barros D., Sall A. S., Gueye O. and Diop L., *Bull. Chem. Soc. Ethiop.*, (1993) 7(2)113 – 115.
- [13] Sall A. S., Diasse-Sarr A., Sarr O. and Diop L., *Main Group. Met. Chem.*, (1992), 15, 6, 265.
- [14] Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3 rd Ed., John Wiley and Sons, (1978) 141.

ANNEXE

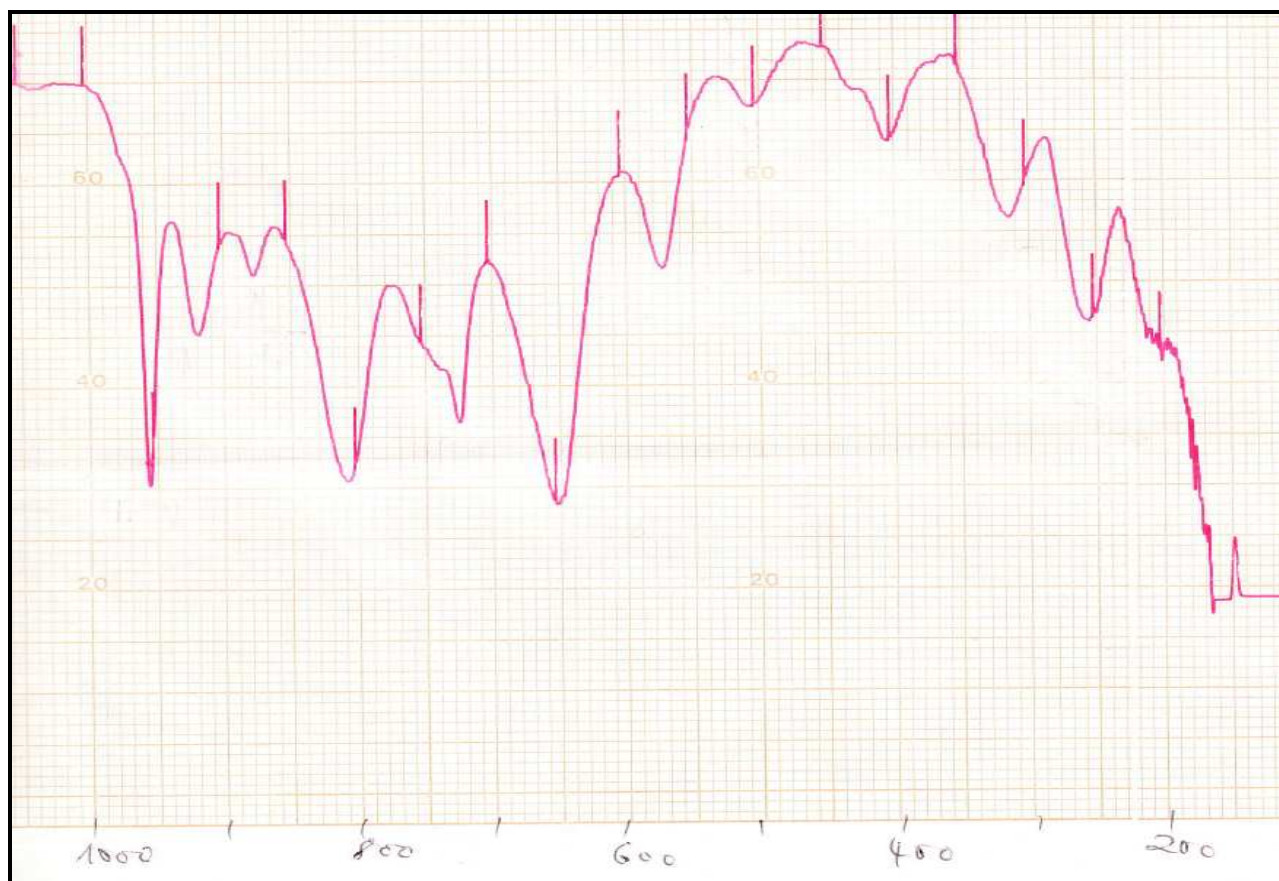
Examples of infrared spectra of some of compounds (S₉, S₂ et S₃)



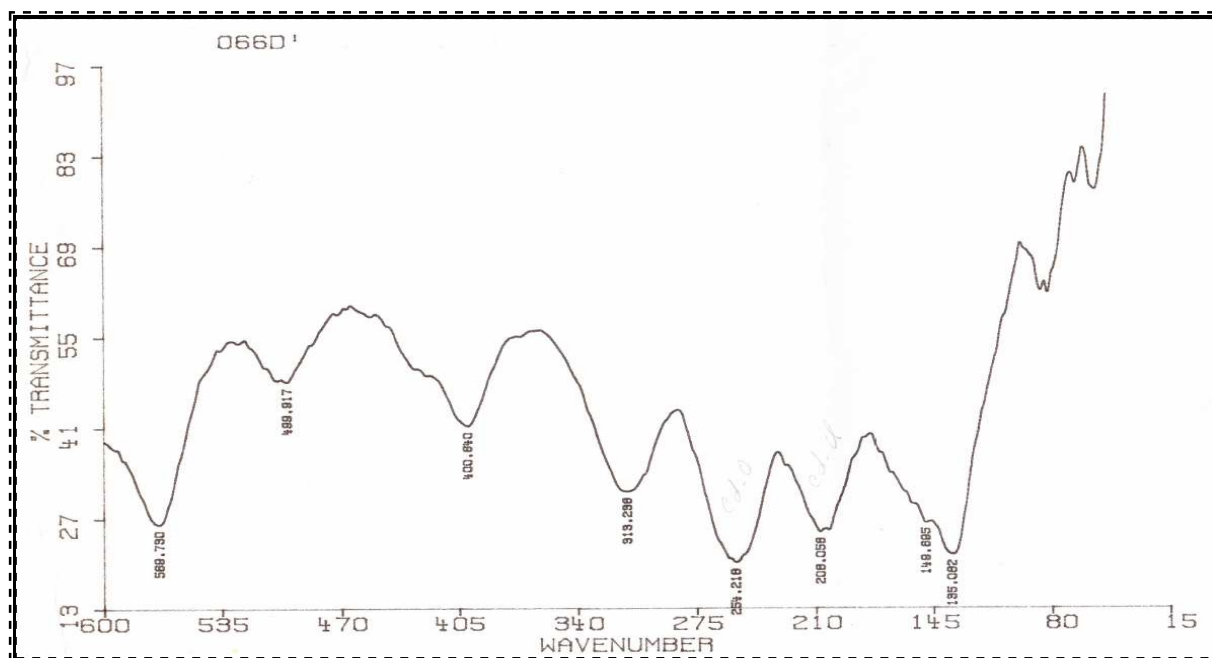
Infrared spectrum of S₂ high frequency



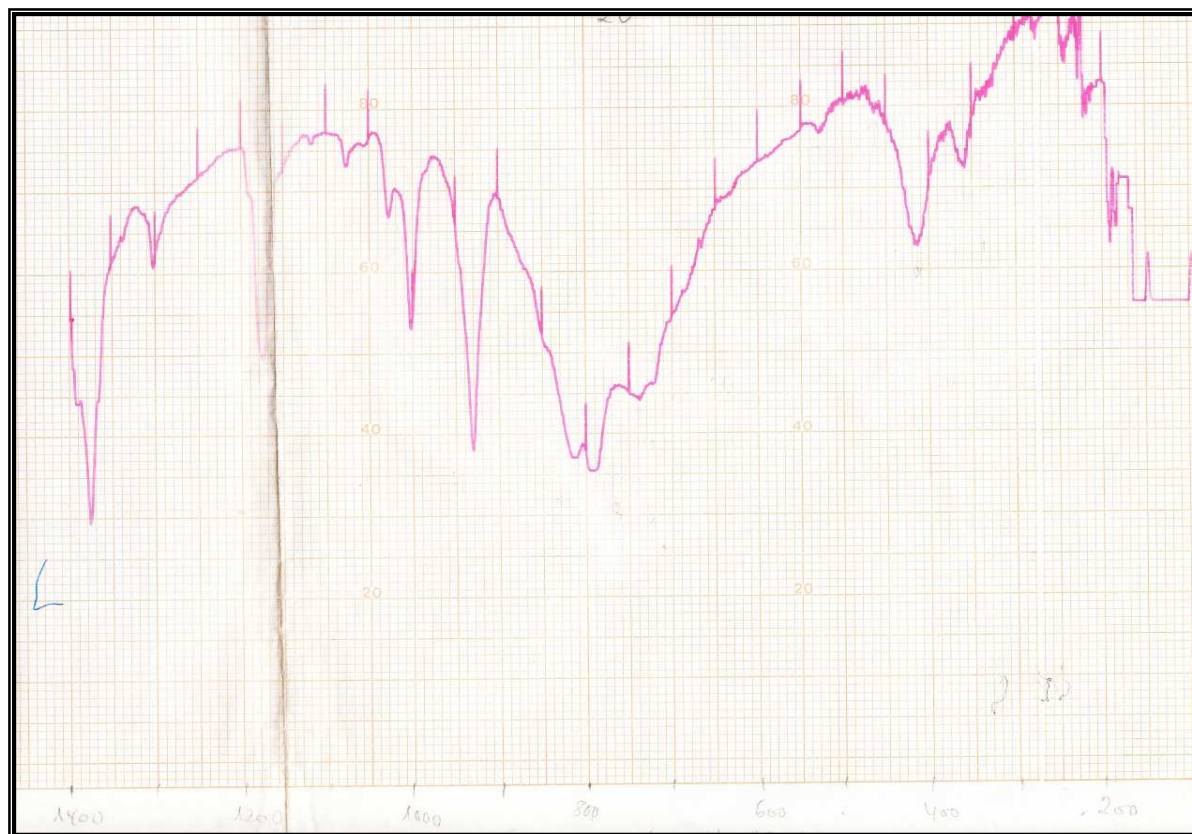
Infrared spectrum of S₂ low frequency



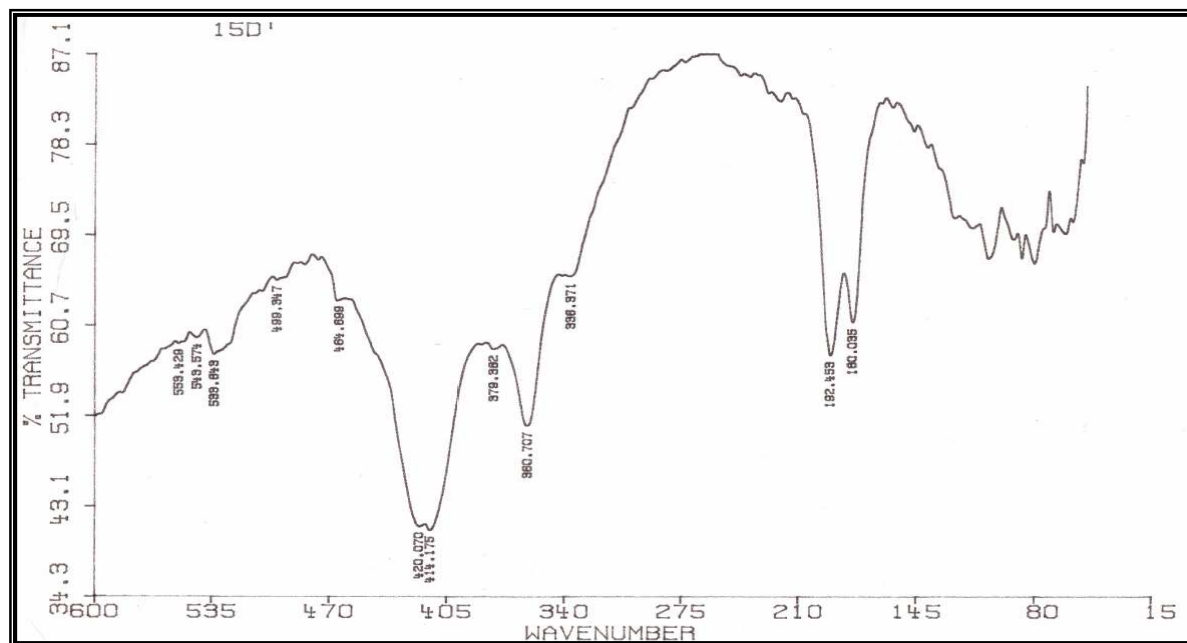
Infrared spectrum of S₉ high frequency



Infrared spectrum of S₉ low frequency



Infrared spectrum of S₃ high frequency



Infrared spectrum of S₃ low frequency