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HYDROGEN BONDING IN SOME 3d HALIDES COMPLEXES WITH FURANNIC OXIMES.

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ملخص :

بينت دراسة الاهتزازات بالأشعة ما تحت الحمراء لمجموعة الهيدروكسيد اختفاء الروابط الهيدروجينية من نوع $O-H...O$ في كل المركبات المعقدة المحصل عليها مع 2-فورفورالدوكسيم (FDH) ومشتقاتها المعوضة في الموقع 5 بمجموعة ميثيل ($M5FDH$) أو بمجموعة إيثيل ($E5FDH$). وكذلك في المركبات المعقدة المكونة مع 3-(2-فوريل) بروبين 2-ألدوكسيم (FAOH) ومع 3-(5-ميثيل 2-فوريل) بروبين 2-ألدوكسيم ($M5FAOH$). من ناحية أخرى ظهرت روابط هيدروجينية داخل الجزيئة من نوع $O-H...X$ ($X = Cl, Br$) في المركبات المعقدة ذات النموذج $[ML_2X_2]$ حيث $L = FAOH, M5FAOH$.

Abstract : The ir study of the hydroxyl vibrations shows there is no hydrogen bond $O-H...O$ for the whole series of compounds obtained with 2-furfuraldoxime (FDH) and its 5 substituted derivatives : 5-methyl ($M5FDH$) or 5-ethyl ($E5FDH$) and with the 3-(2-furyl) 2-propenaldoxime (FAOH) and 3-(5-methyl 2-furyl) 2-propenaldoxime ($M5FAOH$). On the other hand, the presence of intramolecular hydrogen bonds $O-H...X$ ($X = Cl$ or Br) is demonstrated in all $[ML_4X_2]$ complexes and in $[ML_2X_2]$ compounds when $L = FAOH$ or $M5FAOH$.

Résumé : L'étude des vibrations infrarouges de l'hydroxyle montre l'absence de liaisons hydrogène du type $O-H...O$ pour tous les complexes de la 2-furfuraldoxime (FDH) et ses dérivés substitués en 5 par un groupement méthyle ($M5FDH$) ou éthyle ($E5FDH$) et à partir de la 3-(2-furyl) prop-2-ène aldoxime (FAOH) et de la 3-(5-méthyl 2-furyl) prop-2-ène aldoxime ($M5FAOH$). En revanche, il apparaît des liaisons hydrogène intramoléculaires $O-H...X$ ($X = Cl$ ou Br) pour tous les complexes du type $[ML_4X_2]$ et pour les complexes $[ML_2X_2]$ ($L = FAOH, M5FAOH$).

Key words : complexes, oximes, ir spectroscopy, hydrogen bonds.

INTRODUCTION

As a part of our study on the coordinating properties of some furannic aldoximes, we describe here an i.r. study of intramolecular hydrogen bonding in some metallic complexes obtained with the above series of ligands.

2-Furfuraldoxime (FDH) and its 5-substituted derivatives : 5-methyl (M5FDH) and 5-ethyl (E5FDH), 3-(2-furyl) 2-propene aldoxime (FAOH) and 3-(5-methyl 2-furyl) 2-propene aldoxime (M5FAOH), whose structures are shown in Figure 1, react with halides MX_2 ($M = Mn, Fe, Co, Ni, Cu$ and Zn ; $X = Cl$ or Br) to give $[ML_2X_2]$ and $[ML_4X_2]$ species ($L =$ furannic oxime)(1-7). As these ligands have hydroxyl group, it is possible to consider intra or intermolecular hydrogen bonds. 2-furfuraldoxime complexes have been widely studied (8) but, as far as we know, there are no earlier publications dealing with the hydrogen bonding in such compounds.

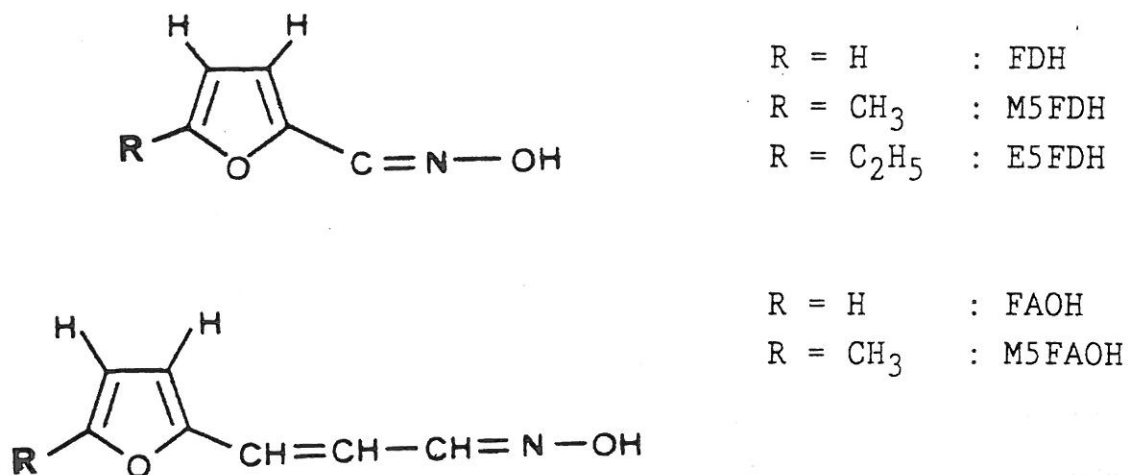


Figure 1 : Furannic ligands structures.

MATERIALS AND METHODS

Syntheses of the complexes :

The complexes were obtained by reacting, in stoichiometric amounts, the oxime and the halide in ethanol or methanol (3-7) : $[ML_2X_2]$ complexes are formed when the reaction temperature is about 80 °C and $[ML_4X_2]$ species when operating at c.a. 4°C. The deuterated oximes were prepared by isotopic exchange, using deuterium oxide to recrystallize the crude oxime. The corresponding deuterated complexes were obtained in absolute ethanol at room temperature (7).

Infrared spectra :

The infrared spectra were recorded with a PE 580 Perkin-Elmer spectrophotometer. The resolution was 2.8 cm^{-1} and the accurate position ($\pm 1\text{ cm}^{-1}$) of the bands was obtained via the Perkin-Elmer 580 Data Station. The low temperature (liquid nitrogen) spectra were recorded from a KBr disk, using a Beckmann "RT2" cryostat. In some cases, carbon tetrachloride was used and the spectra were recorded with a variable thickness cell set at 0.6 mm ; the spectrum of CCl_4 was subtracted from the whole spectra by the computer.

RESULTS AND DISCUSSION

The configuration (E or Z) of the oxime moiety of the ligands was previously determined (2-7) according to Hadzi and Premru (9). When using the synthetic method described by Brady and Goldstein (10), the only FAOH leads to E form, whereas the other oximes give Z form.

As reported in the literature (3, 4, 6), the analysis of the whole i.r. spectra is useful to determine the coordinating atoms in every complex. The main results are :

in the $[ML_4X_2]$ series the monodentate ligand L is bonded through the N atom ; in the $[ML_2X_2]$ series (L = FDH, M5FDH or E5FDH), the coordinating atoms are O-ring and O-oxime and, finally, in the $[ML_2X_2]$ series (L = FAOH or M5FAOH) the chelation occurs through O-ring and N atoms. The i.r. and electronic spectra confirm the trans-octahedral geometry for the whole series of complexes.

In order to establish the presence of hydrogen bonds, we have recorded the following two series of spectra :

- in KBr disk at room temperature and at liquid nitrogen temperature for all compounds ;
- in KBr disks and carbon tetrachloride at room temperature for the ligands, the deuterated ligands and their relative cupric complexes.

In most cases, on cooling, a shift or a splitting of the O-H stretching vibration band is observed in presence of intra- or intermolecular hydrogen bonds. Sometimes, this band is broadened as reported by Lippincott *et al.* (11) and Hadzi and Bratos (12). But this band undergoes no such modifications if there is no hydrogen bonding.

Low temperature i.r. spectra :

The results given in Table 1 show that in each case, the O-H bending vibration band is affected upon cooling. However, the hydroxyl stretching vibration shows several variations according to the type of complex :

- the $[ML_4X_2]$ species show two bands at liquid nitrogen temperature and one at room temperature ;
- the $[ML_2X_2]$ species lead to only one band irrespective of temperature ;

Table 1 : Hydroxyl vibrations, KBr disk (cm^{-1}).
(a) room temperature

COMPOUND	Stretching		Bending	
	r.t.	(a) cooled	r.t.	cooled
$[\text{CuCl}_2(\text{FDH})_2]$	3245	3245	1430-1315	1432-1316
$[\text{CoCl}_2(\text{FDH})_4]$	3255	3247-3227	1430-1325	1429-1321
$[\text{MnCl}_2(\text{M5FDH})_2]$	3336	3331	1427-1319	1426-1319
$[\text{CoCl}_2(\text{M5FDH})_2]$	3403	3403	1431-1324	1434-1321
$[\text{CuCl}_2(\text{M5FDH})_2]$	3227	3227	1428-1320	1435-1325
$[\text{CuBr}_2(\text{M5FDH})_2]$	3242	3231	1426-1330	1429-1330
$[\text{NiCl}_2(\text{M5FDH})_4]$	3278-3237	3280-3235	1431-1323	1432-1320
$[\text{NiBr}_2(\text{M5FDH})_4]$	3277-3246	3278-3238	1418-1321	1435-1320
$[\text{CoCl}_2(\text{M5FDH})_4]$	3273-3247	3281-3236	1431-1324	1434-1321
$[\text{CoBr}_2(\text{M5FDH})_4]$	3274-3251	3275-3235	1420-1321	1420-1322
$[\text{CuCl}_2(\text{E5FDH})_2]$	3224	3222	1428-1323	1425-1324
$[\text{CuBr}_2(\text{E5FDH})_2]$	3245	3243	1426-1325	1429-1326
$[\text{CoCl}_2(\text{E5FDH})_4]$	3266-3221	3264-3220	1433-1325	1431-1326
$[\text{NiCl}_2(\text{E5FDH})_4]$	3263-3215	3263-3214	1432-1325	1429-1326
$[\text{NiBr}_2(\text{E5FDH})_4]$	3263-3225	3266-3224	1422-1324	1422-1325
$[\text{MnCl}_2(\text{FAOH})_2]$	3377	3372	1404-1324	1406-1324
$[\text{CoCl}_2(\text{FAOH})_2]$	3332	3330	1408-1328	1408-1329
$[\text{NiCl}_2(\text{FAOH})_2]$	3329	3324	1407-1324	1408-1323
$[\text{CuCl}_2(\text{FAOH})_2]$	3254	3245	1415-1328	1415-1330
$[\text{CuBr}_2(\text{FAOH})_2]$	3258	3252	1411-1320	1410-1320
$[\text{CoCl}_2(\text{FAOH})_4]$	3337-3276	3352-3263	1414-1325	1417-1322
$[\text{CoBr}_2(\text{FAOH})_4]$	3345-3261	3352-3251	1407-1329	1410-1330
$[\text{NiCl}_2(\text{FAOH})_4]$	3387-3267	3367-3324	1414-1325	1408-1323
$[\text{CoCl}_2(\text{M5FAOH})_2]$	3330	3324	1415-1326	1412-1321
$[\text{CoBr}_2(\text{M5FAOH})_2]$	3413	3408	1422-1323	1423-1323
$[\text{CuCl}_2(\text{M5FAOH})_2]$	3229	3227	1436-1326	1428-1326
$[\text{CuBr}_2(\text{M5FAOH})_2]$	3245	3238	1419-1329	1421-1328

- in the $[ML_2X_2]$ series, the single band remains at the same wavenumber whatever the conditions, ($L = FDH, M5FDH$ or $E5FDH$). It is shifted down on cooling when $L = FAOH$ or $M5FAOH$.

On the basis of these results, we can classify the furannic aldoximes complexes into three groups :

- 1) all $[ML_4X_2]$ species ;
- 2) $[ML_2X_2]$ complexes with $L = FDH, M5FDH, E5FDH$
- 3) $[ML_2X_2]$ complexes with $L = FAOH$ or $M5FAOH$.

These results lead us to the following conclusions :

- 1) there is no hydrogen bonding in the $[ML_2X_2]$ series when $L = FDH, M5FDH$ or $E5FDH$ because $\nu(O-H)$ is not sensitive to cooling ;
- 2) hydrogen bonds are present for $[ML_4X_2]$ complexes and in the $[ML_2X_2]$ series only when $L = FAOH$ or $M5FAOH$.

Spectra of deuterated compounds :

The study of the spectra of deuterated compounds help us to understand the behaviour of the hydroxyl group towards hydrogen bonding. Consequently, these spectra were recorded first with the ligands, and then with cupric chloride complexes. The measurements were made at room temperature which restricts the risks of hydrogen-deuterium exchange. The main data are listed in Table 2.

The wavenumbers of the stretching vibrations $\nu(O-H)$ and $\nu(O-D)$ (KBr disks) are very near the known limits for $O-H...O'$ hydrogen bonds : 3603 and 2654 cm^{-1} respectively in hydrated inorganic compounds (11, 12). We recently obtained some single crystals and the X-ray crystallographic study of $[CoCl_2(FDH)_4]$, $[NiCl_2(FDH)_4]$ and

[CoBr₂(M5FDH)₄] complexes shows that intramolecular hydrogen bonding occurs through the O-H... X system (X = Cl

Table 2 : Deuterated compounds spectra (cm⁻¹).

^a KBr disk

^b CCl₄ suspension

COMPOUND	ν (O-H)	ν (O-H)	ν (O-D)	ν (O-D)
	free	ass.	free	ass.
FDH ^a	-	3285	-	-
FDD ^a	-	3285	2668	2430
[CuCl ₂ (FDH) ₂] ^a	-	3245	-	-
[CuCl ₂ (FDD) ₂] ^a	3589	3469	2655	2417
[CuCl ₂ (FDD) ₂] ^b	3598	3470	2656	2418
M5FDH ^a	-	3272	-	-
M5FDD ^a	-	3172	-	2317
[CuCl ₂ (M5FDH) ₂] ^a	-	3227	-	-
[CuCl ₂ (M5FDD) ₂] ^a	-	3465	2538	2345
[CuCl ₂ (M5FDD) ₂] ^b	3586	3275	2533	2405
E5FDH ^a	-	3187	-	-
E5FDD ^a	-	3183	2594	2316
[CuCl ₂ (E5FDH) ₂] ^a	3594	3224	-	-
[CuCl ₂ (E5FDD) ₂] ^a	-	3220	2588	2403
[CuCl ₂ (E5FDD) ₂] ^b	3471	3227	2563	2403
FAOH ^a	3586	3177	-	-
FAOD ^a	-	3220	2547	2352
[CuCl ₂ (FAOH) ₂] ^a	-	3254	-	-
[CuCl ₂ (FAOD) ₂] ^a	-	3257	2592	2400
[CuCl ₂ (FAOD) ₂] ^b	-	3257	2585	2428
M5FAOH ^a	-	3166	-	-
M5FAOD ^a	-	3430	2655	2241
[CuCl ₂ (M5FAOH) ₂] ^a	-	3229	-	-
[CuCl ₂ (M5FAOD) ₂] ^a	3386	3241	2509	2405
[CuCl ₂ (M5FAOD) ₂] ^b	3510	3226	2575	2405

or Br) and not through the O-H...O moiety (13); the lengths of these bonds (2.998 and 3.003 Å) are similar to those previously described (14).

Table 3 : Metal-halogene stretching vibration, KBr disk (cm^{-1}). (a) room temperature

COMPOUND	ν (M-X) r.t. (a)	ν (M-X) cooled
$[\text{CuCl}_2(\text{M5FDH})_2]$	255	256
$[\text{CoCl}_2(\text{M5FDH})_2]$	325	327
$[\text{CoCl}_2(\text{M5FDH})_4]$	316	328
$[\text{CuCl}_2(\text{E5FDH})_2]$	272	276
$[\text{CuCl}_2(\text{FAOH})_2]$	255	265
$[\text{CuCl}_2(\text{M5FAOH})_2]$	249	265

If we examine the representative metal-halogen stretching vibrations reported in Table 3, we find again the same three groups :

- $[\text{ML}_2\text{X}_4]$ species : the $\nu(\text{M-Cl})$ vibration band is shifted to higher wavenumbers on cooling ;
- $[\text{ML}_2\text{X}_2]$ complexes (L = M5FDH or E5FDH) : the metal-halogen stretching band is not significantly affected ;
- $[\text{ML}_2\text{X}_2]$ complexes (L = FAOH or M5FAOH) : on cooling, the $\nu(\text{M-Cl})$ vibration band is shifted up.

CONCLUSION

On the basis of the present study , the complexes may be classified according to their intramolecular hydrogen bonds :

- hydrogen bonds are present in the $[ML_4X_2]$ series. As there are not any O-H...O bonds, hydrogen bonding is through O-H...X ;
- in the case of $[ML_2X_2]$ compounds (L = FDH, M5FDH or E5FDH) there is no hydrogen bonding because the $\nu(O-H)$ vibration bands are not shifted, splitted or broadened at liquid nitrogen temperature.
- finally, in the $[ML_2X_2]$ complexes (L = FAOH, M5FAOH), there is also the presence of O-H...X hydrogen bonding.

A detailed crystallographic study of these complexes will soon be published (13).

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