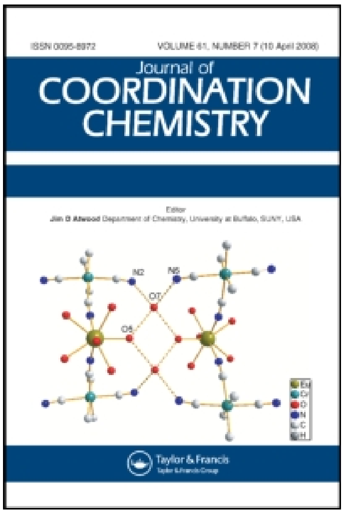

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METALLIC COMPLEXES OF FURAN OXIMES II[1] COMPLEXES OF ß-FURFURALDOXIME WITH CADMIUM(II) HALIDES

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β-furfuraldoxime (FDH) is a well-known bidentate ligand which coordinates through the O-ring and the O-oxime atoms to give ML_2X_2 complexes where MX_2 is generally a first row transition metal salt ($X = Cl$, Br or pseudohalogen). We describe here complexes obtained with CdX_2 salts ($X = Cl$, Br, I).

Keywords: Fufuraldoxime, cadmium, halides, complexes, synthesis

INTRODUCTION

Although β-furfuraldoxime (*Z* or *anti* form, abreviated here as FDH) is a well-known ligand,[2–11] very few papers deal with its second row transition metal complexes. In 1931, Taylor *et al.*,[2] noted that only the β form of furfuraldoxime reacts with ferric chloride and copper acetate to give metallic complexes. Further, in 1940, Bryson and Dwyer[3] reported the preparation of complexes with FDH and cupric chloride, silver nitrate, silver perchlorate, silver sulphate, nickel(II) chloride and cobalt(II) chloride. In 1941, these authors described new complexes obtained with FDH and palladous and platinous chlorides and again with M(II), Co(II) and Cu(II) chlorides.[4] More recently, Gupta and Bhat obtained an "adduct" with silver nitrate and Pd(II) square-planar complexes.[8] They also studied the formation constants of some β-furfuraldoxime complexes with Cd(II) and UO_2^{2+} without characterization of solid products.[9]

As part of a study to determine the coordination properties of various furan oximes towards transition metal salts, we have synthetized three new complexes with FDH and cadmium(II) halides. We report here the preparation and some properties of these new compounds on the basis of IR and NMR spectra. As far as we know, this is the first report of a ternary iodide complex with FDH.

EXPERIMENTAL

Preparation of β-furfuraldoxime (FDH)

This ligand was obtained by the method described by Brady and Goldstein[12] and purified by recrystallization from water.

Preparation of cadmium(II) chloride and bromide complexes

A slight excess of cadmium halide (0.013 mol) was dissolved in absolute ethanol and heated. When the alcohol was refluxing, a solution of the oxime (0.020 mol) in ethanol was added slowly with stirring. The resulting clear solution was heated until a white solid precipitated. If no precipitate appeared, it was necessary to remove the solvent by distillation until the precipitation occurred. After cooling, the white solid was filtered with suction, washed with absolute ethanol and *n*-pentane (for the $CdCl_2$ derivative) or with cyclohexane (for the $CdBr_2$ derivative) and dried under vacuum at room temperature.

Preparation of the cadmium(II) iodide complex

Cadmium(II) iodide (0.010 mol) was dissolved in absolute ethanol and heated to 60°C. A solution of the oxime (0.020 mol) in methanol was added slowly with stirring. The resulting solution was kept at 60°C for forty minutes and the excess solvent removed by gentle distillation. After cooling, the precipitate was filtered with suction, washed with cyclohexane and dried under vacuum at room temperature.

Physical measurements

The elemental analysis were carried out by the Service de Microanalyse du C.N.R.S. (Vernaison - France). The metal was determined by I.C.P. Spectroscopy (Laboratoire de Pharmacologie, C.H.U. Angers - France). The conductance values were obtained using a Tacussel CD6NG Conductimeter, at 25°C, with 10^{-3} mol.dm^{-3} solution of the complex in absolute ethanol. The infrared spectra were recorded on a Perkin-Elmer 580 in NaCl pellets from 4000 cm^{-1} to 600 cm^{-1} and in nujol suspension between polyethylene windows in the range 600 to 180 cm^{-1}. The NMR spectra were obtained at 60 MHz with a Varian EM 360A instrument at room temperature, with hexadeuteriated DMSO as solvent and tetramethylsilane as internal reference. The chemical shifts are given in ppm and coupling constants in Hertz. The melting points were determined with a Buchi Tottoli apparatus.

RESULTS AND DISCUSSION

Many complexes deriving from β-furfuraldoxime and first row transition metal salts have been synthetized and described. In the cases of $[ML_2]X_2$ or $[ML_2X_2]$ compounds, it has been assumed that the oxime ligand coordinates through the O-ring

TABLE I
Analytical data for the complexes.

Compound	Yield %	Colour	M.P. (°C)	Molar conduct.	Elemental analysis[b] (%)			
					C	H	X	Cd
$[(FDH)_2CdCl_2]$	71	white	> 295	3.9[a]	29.62 (29.55)	2.49 (2.52)	27.77 (27.72)	17.48 (18.52)
$[(FDH)_2CdBr_2]$	27	white	> 295	3.8	24.29 (24.99)	2.04 (2.03)	22.73 (22.08)	32.32 (32.42)
$[(FDH)_2CdI_2]$	20	off-white	> 295	1.7	20.41 (19.37)	1.71 (1.58)	43.13 (44.10)	19.10 (19.67)

[a] Conductance of absolute ethanol: 10^{-8} S cm^3 mol^{-1}; Conductance of NaI (10^{-3} mol dm^{-3} ethanol solution): 33.3 S cm^2 mol^{-2}. [b] Found values in brackets. It was not possible to determine molecular weights because of the compounds are insoluble in common cryoscopic solvents.

TABLE II

Main IR frequencies for the ligand and complexes with assignments according to ref. 14.

Species	O–H stretch.	O–H deform I	O–H deform II	C=N stretch	N–O stretch	C–O–C deform	ring breathing	ring stretch	C–H deform in plane	C–H deform out of plane	M–O oxime	M–O ring
β-FDH	3160 (b) 3040 (b)	1445 (m)	1328 (m)	1645 (s)	963 (s)	1235 (s)	1015 (s)	1565 (m) 1487 (sh) 1380 (s) 892 (m)	1185 (s) 1142 (s) 1085 (s)	920 (m) 875 (w) 820 (b) 747 (s)		
[(FDH)$_2$CdCl$_2$]	3350 (s)	1425 (s)	1321 (m)	1655 (s)	971 (s)	1250 (s)	1029 (s)	1564 (s) 1470 (s) 1378 (s) 902 (w)	1190 (s) 1151 (m) 1085 (s)	930 (s) 882 (w) 820 (s) 756 (s)	655 (m)	490 (m)
[(FDH)$_2$CdBr$_2$]	3360 (s)	1415 (s)	1318 (m)	1650 (s)	969 (s)	1245 (s)	1024 (s)	1561 (s) 1470 (s) 1375 (s) 902 (w)	1190 (s) 1149 (m) 1085 (s)	929 (s) 882 (w) 819 (s) 752 (s)	655 (m)	480 (m)
[(FDH)$_2$CdI$_2$]	3325 (s)	1425 (w)	1321 (s)	1655 (s)	969 (s)	1240 (w)	1024 (s)	1561 (s) 1465 (s) 1370 (s) 882 (m)	1190 (s) 1142 (s) 1090 (s)	929 (s) 904 (m) 819 (s) 760 (s)	658 (m)	463 (m)

and the O-oxime atoms on the basis of IR spectra.[2–11] Usually it is not possible to obtain NMR spectra because the complexes are paramagnetic. However the cadmium derivatives are diamagnetic and NMR spectra can be recorded. Table I summarizes some analytical data for the three new compounds.

On the basis of elemental analysis and molar conductances, the formula of these complexes can be written $[(FDH)_2CdX_2]$, where X = Cl, Br, I. The very weak molar conductance shows that they are quite non-ionic species. These compounds are very stable at room temperature and no decomposition was observed up to 295°C.

Infrared spectra

The main infrared spectral data for the ligand and the three complexes are presented in Table II. First it is noticed that the two broad bands due to O-H stretching in the spectrum of the ligand are shifted to give a strong one in the 3350 cm^{-1} region in the complexes. This peak is not as broad as those in the FDH spectrum. This fact shows clearly that the intramolecular hydrogen bonding of the ligand is broken by complexation. For the vibrations bands due to O-H deformation, C = N stretching, N-O stretching, C-O-C deformation and ring breathing the shifts observed for the Cd(II) complexes are approximately the same as those described for other first row transition metal chlorides with two FDH ligands.[6] In the cadmium derivatives, the exchange of Cl or Br by I does not cause significant modifications in the infrared spectra over the range studied. In the region 200–400 cm^{-1} a weak band appears at 205 cm^{-1} ($CdCl_2$ derivative), 213 cm^{-1} ($CdBr_2$ derivative) this can be assigned to the Cd-X stretch accordingly to Ferraro.[13] For the CdI_2 derivative this band should appear around 180 cm^{-1}.

The complexes also exhibit a sharp band at 490 cm^{-1} ($CdCl_2$), 480 cm^{-1} ($CdBr_2$) and 475 cm^{-1} (CdI_2), attributed to M-O (ring) stretching vibrations.[13]

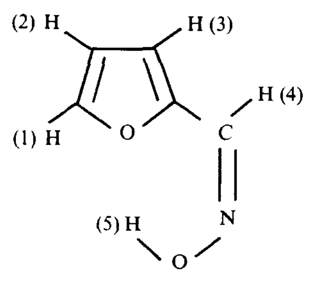
^1H NMR spectra

The chemical shifts of the protons in FDH and its Cd(II) complexes are listed in Table III. They are in good agreement with those observed in the furan series.[15] We notice that coupling constants (see Table III) remain reasonably constant when passing from a free ligand to a coordinated one. The chemical shifts are all shifted to lower field in the complexes; only the signal of the hydroxyl proton H(5) remains approximatively unchanged. This singlet is broad and not well resolved in the FDH spectrum but

TABLE III
^{1} H nmr data for the ligand and its complexes

	Chemical shifts^a (ppm)					Coupling constants (Hz)	
Compound	H(1)	H(2)	H(3)	H(4)	H(5)	$J_{1,2}$	$J_{2,3}$
FDH	7.78	6.68	7.33	7.63	11.76	2.2	3.6
$[(FDH)_2CdCl_2]$	7.68	6.56	7.16	7.43	11.72	2.0	3.7
$[(FDH)_2CdBr_2]$	7.61	6.51	7.08	7.39	11.75	2.1	3.5
$[(FDH)_2CdI_2]$	7.63	6.55	7.20	7.47	11.73	1.9	3.6

^{a}Numbering scheme is shown in diagram



becomes sharp in the spectra of the complexes. This fact can be explained by the disappearance of hydrogen bonding in the complexes as was also suggested by their infrared spectra.

The infrared and proton magnetic resonance spectra shows unambiguously that FDH acts as a bidentate ligand towards cadmium(II) halides as well as with first row transition metal derivatives. The resulting complexes are the non-ionized ones $[(FDH)_2CdX_2]$ (X= Cl, Br or I) and the ligand coordinates through the O-ring and the O-oxime atoms. Attempts to obtain suitable crystals for structure analysis have not yet been successful.

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