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Nickel(II) Complexes of Anti-2-furancarboxaldoxime

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Five different complexes of nickel(II) with *anti*-2-furancarboxaldoxime (β-*FD*H) have been prepared and characterized by elemental analysis, molecular weights, conductance studies, magnetic moments and infra-red spectral studies. These are $[Ni(FDH)_4Cl_2]$, $[Ni(FD)_2(FDH)]$, $[Ni(FD)_2(FDH)_2]$, $[Ni(FD)_2 \cdot en]$, and $[Ni(FD)_2]$. All the complexes are neutral monomeric, paramagnetic ($\mu = 3.3–3.7\ \mu_B$) and may be considered octahedral except the complex $[Ni(FD)_2]$, ($\mu = 2.92\ \mu_B$) which is tetrahedral. In these complexes the ligand functions as a monodentate and/or bidentate, coordinating with furan oxygen and oxime oxygen in the latter case. The ligand has been shown to be present in the ionized, and/or unionized form in these complexes.

The ligand *anti*-2-furancarboxaldoxime (β-*FD*H) is known to form complexes with Pd[1–5], Cu, and Co[6]. *Sen* and *Pickerell*[7] have prepared and characterized the complexes of this ligand with Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Fe(II), Cr(III), and Fe(III) and suggested that the complexes are octahedral on the basis of a stipulation that the ligand functioned as bidentate in all the above complexes except in $[Cr(FDH)_3Cl_3]$ and $[Fe(FDH)_3Cl_3]$ where it functions as monodentate coordinating via the furan oxygen atom. The bidentate ligand molecule can coordinate via the furan oxygen and the oxime oxygen atoms. Infra-red spectral evidence[8] on the above complexes has established the denticity of the ligand, and it supports the above stipulation.

During the course of the present work, the synthesis and characterization of some of the nickel(II) complexes of 2-furancarboxaldoxime (*anti*-form) has been done by elemental analysis, molecular weight determination, conductance data, infra-red spectra and magnetic moment measurements. Although *Byrson* and *Dwyer*[9, 10] prepared a number of complexes of this ligand with Co(II), Co(III), Ni(II), Cu(II), Cu(I), Ag(I), Pd(II), and Pt(II), no detailed study has yet

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been reported on these complexes. They proposed the formulae of these complexes primarily on the basis of metal analysis, and in some cases, molecular weight determinations.

Experimental Part

Reagents and Techniques

Anti-2-furancarboxaldoxime was prepared by reacting freshly distilled furfural with hydroxylamine hydrochloride by the method of *Brady* and *Goldstein*[11]. All other reagents used were of A.R./B.D.H. grade.

Dichlorotetrakis(furancarboxaldoxime)nickel(II), $[Ni(FDH)_4Cl_2]$ (I)

*FD*H (4.44 g; 0.04 mole) dissolved in 25 ml of absol. *Et*OH was added to cold solution of $NiCl_2$ (2.37 g; 0.01 mole) in 75 ml of absol. *Et*OH. The mixture was placed in an ice bath for 15 min. Greenish-white dense crystals were obtained, filtered, washed with *Et*OH and recrystallized from boiling absol. *Et*OH, dried in vacuo over P_2O_5; yield = 5 g (73%).

$[Ni(FDH)_4Cl_2]$: Calc: C 41.83; H 3.49; N 9.76; Cl 12.38; Ni 10.23.
Found: C 41.50; H 3.80; N 9.52; Cl 11.92; Ni 10.28.

Tris(furancarboxaldoxime)nickel(II), $[Ni(FD)_2(FDH)]$ (II)

*FD*H (13.32 g; 0.12 mole) dissolved in 75 ml of *Et*OH was added with stirring to a hot solution (80–90°) of nickel acetate (9.96 g; 0.04 mole) dissolved in 150 ml of water. NH_4OH solution (1 : 1) was then added dropwise till pH became 8.8. The greyish white precipitate obtained was filtered, washed with aq. alcohol, recrystallized from benzene and dried in vacuo at 100 °C over P_2O_5; yield = 14 g (88%).

$[Ni(FD)_2(FDH)]$ Calc.: C 46.07; H 3.33; N 10.75; Ni 15.02.
Found: C 45.80; H 3.90; N 10.10; Ni 14.78.

Tetrakis(furancarboxaldoxime)nickel(II), $[Ni(FD)_2(FDH)_2]$ (III)

*FD*H (1.11 g; 0.01 mole) was added to a solution of complex (II) (3.9 g; 0.01 mole) dissolved in 30 ml of benzene. The solution was concentrated by evaporating the benzene at room temp. On scratching brown needle shaped crystals were obtained. These were filtered, washed with aq. *Et*OH, recrystallized from benzene, and dried in vacuo over P_2O_5; yield = 4.5 g (90%).

$[Ni(FD)_2(FDH)_2]$ Calc.: C 47.84; H 3.59; N 11.16; Ni 11.70.
Found: C 47.02; H 3.80; N 11.00; Ni 11.85.

Ethylenediaminebis(furancarboxaldoxime)nickel(II), $[Ni(FD)_2en]$ (IV)

Complex (II) (3.9 g; 0.01 mole) was dissolved in 50 ml of benzene and ethylenediamine (0.6 g; 0.01 mole) dissolved in 5 ml of benzene was added with stirring. After continuous stirring for 15 min the light brown crystals obtained were filtered, washed with benzene and dried in vacuo over P_2O_5; yield = 2.5 g (73.5%).

[Ni(*FD*)$_2$*en*] Calc.: C 41.52; H 4.72; N 16.54; Ni 17.33.
Found: C 40.80; H 5.1; N 15.89; Ni 17.03.

Bis(furancarboxaldoxime)nickel(II), [Ni(*FD*)$_2$] (V)

To a clear solution of complex (II) (3.9 g; 0.01 mole) in 50 ml of cold pyridine was added cold water when semi-colloidal yellowish precipitate was obtained. The precipitate was coagulated by addition of 1 g of sodium acetate. It was filtered, washed with water, recrystallized from acetone and dried under vacuo over P_2O_5 for 6 hours at 146 °C, yield = 2 g (71%).

[Ni(*FD*)$_2$] Calcd.: C 43.06; H 2.87; N 10.05; Ni 21.06.
Found: C 42.5; H 3.2; N 9.92; Ni 20.82.

Physical Measurements

Melting points: Melting points were measured using a calibrated thermometer.

Molecular weights: Molecular weights were determined cryoscopically in purified nitrobenzene[12]. The freezing point depression constant of the solvent was determined using benzil ($10^{-2}M$).

Conductance measurements: These were made in purified nitrobenzene on a bridge (Leeds & Northrup).

Magnetic moment measurements: These were done on *Gouy* balance taking Hg[Co(CNS)$_4$] as the standard, and the diamagnetic corrections[13] for the ligand moiety were made.

Infra-red spectra: Perkin Elmer spectrophotometer model 621 was used for taking the infra-red spectra using CsI disc technique.

Results and Discussion

The various complexes formed by 2-furancarboxaldoxime (*anti*-form) with nickel(II) are summarized in Table 1, where the colour, m.pt., mol.wt., magnetic moment and molar conductance of these complexes are also reported. All the complexes have been found to be paramagnetic and neutral and monomeric in nitrobenzene. The complexes may be considered under three categories, those containing only unionized (neutral) ligand molecules (complex I), those that contain both unionized as well as ionized ligand molecules (complexes II and III) and finally those containing only ionized ligand molecules (complexes IV and V).

On adding β-*FD*H to nickel chloride solution in absolute ethanol at ice temperature, a greenish white crystalline complex [Ni(*FD*H)$_4$Cl$_2$] (I) is obtained. The conductance measurements in nitrobenzene indicate it to be a non-electrolyte species, and thus chlorine may be considered as part of coordination sphere. The magnetic moment value of 3.29 μ_B suggests the presence of two unpaired electrons in nickel(II), and the complex could thus be octahedral proveded that β-*FD*H acts as a monodentate ligand. The evidence for the denticity of the ligand has been obtained from the IR studies of the complex (Tables 2 and 3). Firstly the broad bands for O—H stretching vibrations at 3160 and 3040 cm^{-1} in the ligand, which indicate the presence of intramolecular hydrogen bonding in it are shifted to strong peak at 3230 cm^{-1} in this complex. This implies that the hydrogen bonding has been partly weakened as a result of complexation. Secondly the additional band in the region 670–630 cm^{-1} in the spectra of the complex are absent in the ligand spectrum. These additional bands are likely to be due to the Ni—O stretching vibrations. Finally C=N-stretching frequency in the ligand at 1640 cm^{-1} shifts to 1652 cm^{-1} in the complex; therefore it may be concluded that the ligand acts as monodentate in this complex and the bonding is likely to be through the oxime oxygen. Ni—Cl stretching vibrations in this complex could not be assigned as the ligand had a band in the usual Ni(II)—Cl sensitive region. Two possible geometrical isomers of the octahedral complex $[\mathrm{Ni}(\mathit{FD}\mathrm{H})_4\mathrm{Cl}_2]$ could then exist corresponding to the position of the two chlorine atoms being either *cis* or *trans*.

Table 1

No.	Complex	Colour	m. pt. (°C)	Mol. Wt.		Molar Conductance in nitrobenzene, Λ_M, Ohm^{-1}, cm^2, mole^{-1}	μ_{eff} μ_B
				Calc.	Found		
I.	$[\mathrm{Ni}(\mathit{FD}\mathrm{H})_4\mathrm{Cl}_2]$	Greenish white	204—207° d	574	*	0.71	3.29
II.	$[\mathrm{Ni}(\mathit{FD})_2(\mathit{FD}\mathrm{H})]$	Greyish white	148—150° d	391	380	0.35	3.42
III.	$[\mathrm{Ni}(\mathit{FD})_2(\mathit{FD}\mathrm{H})_2]$	Brown	137—139°	502	495	0.41	3.73
IV.	$[\mathrm{Ni}(\mathit{FD})_2 \cdot \mathit{en}]$	Light brown	118—120°	339	317	0.52	3.51
V.	$[\mathrm{Ni}(\mathit{FD})_2]$	Greenish yellow	> 250°	279	260	0.21	2.92

d = decomposes.

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* Not sufficiently soluble for the determination.

In the second category of Ni(II) complexes of β-*FD*H, the complex $[\mathrm{Ni}(\mathit{FD})_2(\mathit{FD}\mathrm{H})]$ is prepared by taking one mole of Ni^{2+} ions and three moles of the ligand in aq. soln. and then raising the pH to 8.8 by adding $\mathrm{NH_4OH}$ soln. This preparation method indicates that two moles of the ligand might ionize at this pH to give the above complex. The conductance data in nitrobenzene indicates that it is a non-electrolyte, and the magnetic moment value of 3.42 μ_B corresponds

Table 2. *IR frequencies of* β-*FDH* * *and its complexes*

Assignments	*FD*H	Ni(*FD*H)$_4$Cl$_2$	Ni(*FD*)$_2$(*FD*H)	Ni(*FD*)$_2$(*FD*H)$_2$	Ni(*FD*)$_2$ · *en*	Ni(*FD*)$_2$
O—H str.	3160 b 3040 b	3230 s	3100 m	3150 m	—	—
O—H deformation	1448 w	1435 m	1400 vw	1406 w	—	—
	1323 s	1325 s	1319 m	1320 m		
$>$C=N str.	1640 m	1652 m	1653 m	1651 m	1658 m	1655 m
=N—OH str.	970 m	975 m	974 w	973 w	965 w	975 w
Ni(II)—O str.	—	6683 s 640 s	380 b	390 b	380 b	380 b

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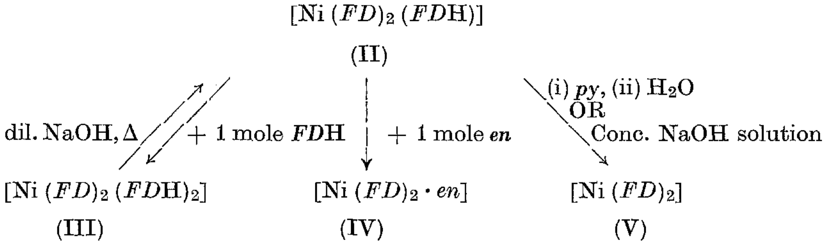
* Assignment of the various frequences of β-*FD*H has been done as described earlier[8].

to two unpaired electrons. [Ni(FD)$_2$(FDH)] may therefore be octahedral with the ligand acting as bidentate bonding through furan and oxime oxygens. Two of the ligand molecules are present in the ionized form while the third is present in the unionized form and is not as strongly bonded to the metal ion as the ionized ones; the latter ligand moiety can be lost under mild alkaline conditions in the following manner:



On reacting 1 mole of the ligand with 1 mole of the complex (II) in benzene solutions, [Ni(FD)$_2$(FDH)$_2$] is obtained. Conductance measurement shows that it is a neutral species, and the magnetic moment is 3.73 μ_B, indicating that it contains two unpaired electrons and hence it is octahedral with the two ionized ligand molecules acting as bidentate while the two unionized ligand molecules act as monodentate.

The evidence for the presence of the ligand in the unionized form in the complexes (II) and (III) is shown by the presence of a medium band in the IR spectra of these compounds at 3100 and 3150 respectively. The C=N-stretching frequency at 1640 cm^{-1} in the ligand gets shifted to 1653 and 1651 cm^{-1} in the complexes (II) and (III) respectively. A broad band at 380 and 390 cm^{-1} in the complexes (II) and (III) respectively can be attributed to Ni(II)—O stretching vibrations as this band is absent in the ligand spectrum. The stretching vibration of Ni(II)—O band is exhibited at 405 cm^{-1} in hexaaquo nickel(II) ion[14] and at 425 and 375 cm^{-1} in nickel(II) methoxide[15]. It is, however, not possible to say whether the M—O bond involves the furan or the oxime oxygen in compound (III), when the ligand acts as monodentate molecule. The band in the region 650 cm^{-1}, also attributed to M—O bond[8] is not observed in the two cases.

The complex with purely ionized ligand molecules, [Ni(FD)$_2$ · en] is obtained from [Ni(FD)$_2$(FDH)] by the replacement of one FDH molecule with one ethylenediamine molecule. The conductance measurements in nitrobenzene indicate that it is a neutral complex and the magnetic moment value of 3.51 μ_B suggests the presence of two unpaired electrons in nickel(II). Therefore [Ni(FD)$_2$ · en] may be octahedral with the ligand, FDH acting as bidentate, bonding through

Table 3. *IR frequences of* β-*FD*H *and its complexes*

Assignments	*FD*H	Ni(*FD*H)$_4$Cl$_2$	Ni(*FD*)$_2$(*FD*H)	Ni(*FD*)$_2$(*FD*H)$_2$	Ni(*FD*)$_2$ · *en*	Ni(*FD*)$_2$
Ring stretching	1565 w	1564 vs	1565 w	1565 w	1565 m	1550 w
	1480 s	1478 s	1477 s	1476 s	1474 s	1475 s
	1380 s	1380 vs	1375 m	1370 m	1370 w	1370 m
	1240 vs	1240 vs	1238 m	1237 m		1228 m
	895 w	903 m	900 w			
Ring breathing	1020 vs	1023 s	1009 m	1007 m	1011 vs	1010 m
C—H in plane deformation	1190 s	1192 vs	1185 s	1182 s	1190 sh	1183 s
	1149 vs	1149 vs	1145 m	1142 m	1150 m	1145 m
	1088 vs	1088 vs	1084 m	1082 m	1080 m	1082 m
C—H out of plane deformation	923 w	937 s	925 w	926 s	930 sh	928 m
	880 sh	888 w	885 sh	884 sh		883 sh
	820 b	826 s	820 m	820 b	815 b	825 b
	750 s	752 s	746 m	747 m	746 s	747 s
Extra bands	590 sh	593 m				
	576 s	574 s	576 s	575 s	574 w	573 s
	570 sh	340 b				
	335 vw					

furan and oxime oxygens. That the ligand is present in the ionized form in this complex is shown by the absence of O—H deformation bands at 1448 and 1323 cm^{-1} in the IR spectrum while the C=N-stretching of frequency at 1640 cm^{-1} in the ligand gets shifted to 1658 cm^{-1} in this complex. Again a broad band at 380 cm^{-1}, found in this compound, could be assigned for Ni(II)—O stretching vibrations. The presence of ethylenediamine is shown in the IR spectrum of this complex, the assignments of which have been made on the basis of earlier studies on ethylenediamine[16]. A broad band at 500 cm^{-1} is assigned to Ni(II)—N stretching vibrations, on the basis of a similar assignment at 515 cm^{-1} in $[\mathrm{Ni}(en)_3]^{2+}$ complex ion[17].

The neutral complex, $[\mathrm{Ni}(FD)_2]$, containing the purely ionized ligand molecules is formed by the removal of one *FD*H molecule from $[\mathrm{Ni}(FD)_2(FD\mathrm{H})]$ by treating it with a base. From the behaviour of similar ligands, it would seem likely that such a species should be diamagnetic containing a square planar four coordinate nickel(II) complex. However, such a compound is not readily obtained by the reaction of nickel(II) salts with 2-furancarboxaldoxime even in the presence of a strong base. Its conductivity in nitrobenzene verifies its nonionic nature and the magnetic moment of the solid (2.92 μ_B) suggests a tetrahedral structure. The IR spectrum of this compound shows the absence of O—H stretching and deformation vibrational bands, and the C=N-stretching frequency is observed at 1655 cm^{-1}. Also there is a broad band at 380 cm^{-1} corresponding to the Ni(II)—O stretching vibrations. Hence it can be concluded that the complex $[\mathrm{Ni}(FD)_2]$ is tetrahedral with the two ionized *FD*H molecules acting as bidentate ligand, coordinating through the furan and the oxime oxygen.

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