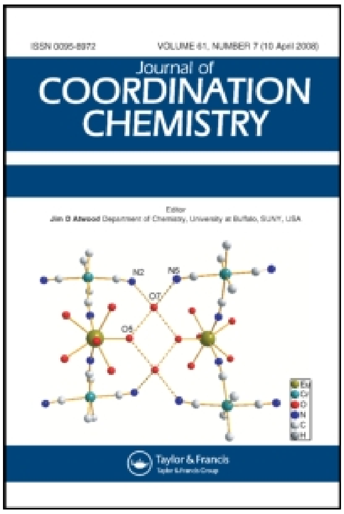

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SYNTHESIS AND CHARACTERIZATION OF ANTI-2-FURAN CARBOXALDOXIME COMPLEXES WITH COBALT(II), COPPER(II & I) AND SILVER(I)

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The ligand, 2-furan carboxaldoxime exists in two geometrical isomeric forms: anti-(β-form) and syn-(α-form). Six different complexes of Co(II), Cu(II), Cu(I) and Ag(I) with anti-2-furan carboxaldoxime (FDH) have been prepared and characterized by elemental analysis, molecular weights, conductance studies, magnetic moments and infra-red spectral studies. These are $[Co(FDH)_4Cl_2]$, $[Co(FD)_2]$, $[Cu(CH_3COO)_2(FDH)]_2$, $[Cu(FD)(OH)]_2$, $Cu(FDH)_2Cl$ and $AgNO_3 \cdot 2FDH$. Under the similar conditions, syn- form does not form any complex with these metal ions. The complexes $[Co(FDH)_4Cl_2]$ and $[Co(FD)_2]$ are neutral, monomeric and para-magnetic (μ = 4.88 and 4.52 BM respectively); the former may be considered as octahedral with FDH acting as monodentate, and the latter as tetrahedral with FD^- as a bidentate ligand. Both the Cu(II) complexes are neutral, dimeric, weakly para-magnetic (μ = 0.44 and 0.28 BM respectively) with the bridging acetato groups in $[Cu(CH_3COO)_2(FDH)]_2$ and with bridging hydroxo groups in $[Cu(FD)(OH)]_2$. The Cu(I) complex may be polymeric, being insoluble in most solvents. The Ag(I) compound is cationic 1:1 electrolyte in nitrobenzene. In all these complexes the ligand functions as monodentate and/or bidentate, coordinating with furan oxygen and oxime oxygen in the latter case. The C–O–C stretching frequency of furan may be taken as the criterion for the denticity of this ligand which is observed at 1240 cm^{-1} (in the free ligand). A shift to lower frequency is observed in the complex if the ligand acts as bidentate. However this frequency is not affected if the ligand acts as monodentate coordinating through the oxime oxygen atom. The ligand has been shown to be present in the ionized and/or unionized form in these complexes.

INTRODUCTION

Since the oxygen atom of the furan ring has a lone electron pair, it should be capable of forming coordination compounds with at least the transition metal ions and, in fact, the metal complexes of furildioxime[1-2], tetrahydrofuran[3-4], tetrahydrofuroic acid[5] and tetrahydroacetic acid[5] etc. are well known. Studies on metal chelates formed from 2-furan carboxaldehyde[6] and its derivatives led to some interesting observations relating to bonding and stereochemistry in the molecules. So it was thought of interest to further this study using 2-furan carboxaldoxime as a chelating agent. However anti-2-furan carboxaldoxime (FDH) has been reported to form octahedral complexes with several bivalent and tervalent metal ions.[7] It has been stipulated that in the complexes of the type $[M(FDH)_2Cl_2]$, where M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) the ligand functions as bidentate coordinating through furan oxygen and oxime oxygen, and as monodentate in $[M(FDH)_3Cl_3]$ where M = Fe(III) and Cr(III) coordinating through the furan oxygen atom. In our earlier work on these complexes the denticity of the ligand has been established by means of infrared spectral studies.[8] Nickel(II) complexes,[9] and the stability constants of U(VI) and Fe(III) complexes[10] with this ligand have also been reported. Bryson *et. al.*[11] and Taylor *et. al.*[12] prepared some complexes of this ligand with Co(II), Ni(II), Cu(II), Cu(I), Ag(I), Pd(II) and Pt(II), but no detailed study has yet been reported on these complexes. The formulae of these complexes were proposed primarily on the basis of metal analysis, and in some cases, molecular weight determination and no definite conclusions could be drawn regarding their structures.

The aim of the present work was, therefore, to prepare and characterize the complexes of Mn(II),

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Cr(III), Fe(II), Fe(III), Co(III), Co(II), Cu(II), Cu(I), Zn(II), Ag(I) etc. with anti-2-furan carboxaldoxime (FDH) by means of elemental analysis, molecular weight determination, conductance data, magnetic measurements and infrared spectral studies. Indeed complexes only with Co(II), Cu(II), Cu(I) and Ag(I) could be prepared. It is interesting to note that Cu(II) complexes reported herein are dimeric in solution as is indicated by molecular weight determinations; they are very weakly paramagnetic in the solid state, which indicates their dimeric formulation even in the solid state.

EXPERIMENTAL

Reagents and Chemicals

Anti-2-furan carboxaldoxime (FDH) was prepared by reacting freshly distilled furfural with hydroxylamine hydrochloride by the method of Brady and Goldstein.[13] All the solvents were purified and dried before use by the standard methods described by Vogel.[14] All other reagents used were of AnalaR or LR (BDH) grade.

Preparation of Complexes

Dichlorotetrakis(2-furan carboxaldoxime)cobalt(II), $[Co(FDH)_4Cl_2]$ FDH (4.44 g; 0.04 mole) dissolved in 25 ml of absolute ethanol was added to a cold solution of cobalt(II) chloride hexahydrate (2.36 g; 0.01 mole) in 50 ml of absolute ethanol in an atmosphere of nitrogen. The mixture was stirred and placed in an ice bath for 30 minutes. The orange red crystals thus obtained were filtered, washed first with a 5 ml portion of cold ethanol and then with n-pentane and dried under *vacuo* over P_2O_5. Yield, 5 g (73%).

Anal. found: C, 41.60; H, 3.30; N, 9.59; Cl, 11.94; Co, 10.11. Calcd. for $[Co(FDH)_4Cl_2]$: C, 41.81; H, 3.48; N, 9.78; Cl, 12.27; Co, 10.28.

Bis(2-furan carboxaldoximato)cobalt(II), $[Co(FD)_2]$ FDH (2.22 g; 0.02 mole) dissolved in 15 ml of ethanol was added with stirring to a solution of cobalt(II) acetate (2.49 g; 0.01 mole) in an atmosphere of nitrogen. The brown precipitate obtained was digested on a water bath for half an hour, filtered, washed with 50% aqueous ethanol and dried in vacuo over P_2O_5. Yield, 2 g (77%).

Anal. found: C, 43.75; H, 3.10; N, 9.82; Co, 20.85. Calcd. for $[Co(FD)_2]$: C, 43.01; H, 2.93; N, 10.04; Co, 21.14.

μ-Tetraacetatobis(2-furan carboxaldoxime) dicopper(II), $[Cu(CH_3COO)_2(FDH)]_2$ FDH (2.22 g; 0.02 mole) dissolved in 15 ml of ethanol was added with stirring to an aqueous solution of copper(II) acetate monohydrate (4.0 g; 0.02 mole). The dark green precipitate obtained was filtered, washed first with water, then with ethanol and finally dried under vacuo over P_2O_5 at 100°C. Yield, 5.5 g (94%).

Anal. found: C, 36.51; H, 3.44; N, 5.58; Cu, 21.98. Calcd. for $[Cu(CH_3COO)_2(FDH)]_2$: C, 36.93; H, 3.76; N, 4.79; Cu, 21.71.

μ-Dihydroxobis(2-furan carboxaldoximato) dicopper(II), $[Cu(FD)(OH)]_2$ To a solution of $CuCl_2 \cdot 2H_2O$ (3.4 g; 0.02 mole) in 50 ml of methanol, added FDH (2.22 g; 0.02 mole) and this was followed by the addition of methanolic sodium acetate solution. To the brown solution thus obtained, about 50 ml of water was added. On stirring the solution, a dark green precipitate was obtained. It was washed first with water, then with alcohol, and dried under vacuo over P_2O_5 at 100°C. Yield, 3 g (79%).

Anal. found: C, 31.33; H, 2.92; N, 7.51; Cu, 33.21. Calcd. for $[Cu(FD)(OH)]_2$: C, 31.50; H, 2.63; N, 7.35; Cu, 33.34.

Bis(2-furan carboxaldoxime)copper(I) chloride, $Cu(FDH)_2Cl$ To a suspension of copper(I) chloride (0.99 g; 0.01 mole) in 25 ml of ethanol, FDH (2.22 g; 0.01 mole) dissolved in 15 ml of ethanol was added in an atmosphere of nitrogen. The whole mass was shaken well, when a heavy crystalline precipitate was obtained. It was filtered (under nitrogen atmosphere), washed with alcohol, and dried in vacuo over P_2O_5. Yield, 3 g (93.5%).

Anal. found: C, 36.80; H, 3.01; N, 8.02; Cu, 20.41; Cl, 10.82. Calcd. for $Cu(FDH)_2Cl$: C, 37.38; H, 3.11; N, 8.72; Cu, 19.81; Cl, 11.59.

Silver nitrate-2-furan carboxaldoxime adduct, $AgNO_3 \cdot 2FDH$ To a solution of silver nitrate (1.7 g, 0.01 mole) in 30 ml of water, added FDH (2.22 g; 0.02 mole) dissolved in 10 ml of ethanol. The crystalline precipitate thus obtained was filtered, washed with cold water. It was recrystallized from hot water, and dried in vacuo over P_2O_5. Yield, 2.8 g (71.4%).

Anal. found: C, 30.60; H, 2.30; N, 10.51; Ag, 28.05. Calcd. for $AgNO_3 \cdot 2FDH$: C, 30.06; H, 2.53; N, 10.71; Ag, 27.55.

Attempts were also made to prepare tris(2-furan carboxaldoximato)cobalt(III) from cobalt chloride using H_2O_2 as the oxidant, and from sodium cobaltinitrite by the method reported earlier,[11] but the complex could not be obtained by either method in a pure form.

Quantitative Elementary Analysis of the Complexes

Carbon and hydrogen were determined simultaneously by the combustion process and the nitrogen estimation were carried out by the usual Kjeldahl's method. Chlorine, silver, cobalt and copper were estimated gravimetrically[15] as AgCl, $CoSO_4$ and CuSCN respectively after decomposing the complexes with nitric acid.

Physical Measurements

Melting points Melting points were taken with a Toshniwal Melting Point apparatus. The thermometer was calibrated, and the reported melting points were corrected.

Molecular weights Molecular weights were determined cryoscopically in purified nitrobenzene[16] solution. The freezing point depression constant of the solvent was determined using benzil (10^{-2}M).

Conductance measurements These were made in purified nitrobenzene solutions (1.0×10^{-3}M) at 25°C on a conductivity bridge (Leeds & Northrup) using a cell with a cell constant 0.095 cm^{-1} at 25°C.

Magnetic moment measurements These were carried out on a Gouy balance at 25°C taking mercuric tetrathiocyanatocobaltate(II), $Hg[Co(CNS)_4]$ as the standard, and diamagnetic corrections[17] for the ligand moiety were made.

Infrared spectra Perkin-Elmer Spectrophotometer model 621 was used for recording the infrared spectra using CsI disc technique.

NMR spectra The nuclear magnetic resonance spectra were recorded on a Varian A-60 NMR Spectrometer using tetramethylsilane as the internal standard.

Ion exchange studies A strong cation exchange resin 4765 (E Merck) and anion exchanger IR-45 (OH) (Rohm & Hass) were used.

RESULTS AND DISCUSSION

The various complexes of anti-2-furan carboxaldoxime studied are summarized in Table I, where the colour, melting point, molecular weight, magnetic moments, and molar conductances are reported. The infrared spectral data are presented in Table II and III which indicate that as a result of coordination, there is (a) appearance of some new bands, (b) frequency shifts of the bands of the coordinated atoms and (c) intensification of some of the bands in the ligand spectrum. The different complexes are discussed here separately.

[Co(FDH)$_4$Cl$_2$] On adding β–FDH to cobalt(II) chloride solution in absolute ethanol at ice cold temperature, an orange red crystalline complex $[Co(FDH)_4Cl_2]$ (I) is obtained. The conductance measurements in nitrobenzene indicate it to be a non-electrolyte species, and thus the chlorine atoms may be considered as a part of the coordination sphere. The magnetic moment of 4.88 BM suggests

TABLE I

No.	Complex	Colour	M. pts. (°C)	Mol. wt.		Molar conductance in nitrobenzene ΛM, $Ohm^{-1} cm^2 mole^{-1}$	μ_{eff} B.M.
				Found	Calcd.		
I	$[Co(FDH)_4Cl_2]$	Orange-red	190–92°	561	574	0.91	4.88
II	$[Co(FD)_2]$	Brown	210–12°	267	279	0.25	4.52
III	$[Cu(CH_3COO)_2(FDH)]_2$	Dark-green	159–61°	541[b]	585	0.37	0.44
IV	$[Cu(FD)(OH)]_2$	Dark-green	193–96°	359	381	0.33	0.28
V	$Cu(FDH)_2Cl$	White	>200°	a	321	a	Diamagnetic
VI	$AgNO_3 \cdot 2FDH$	White	128–29°	201	392	95.41	Diamagnetic

[a] Highly insoluble in common solvents.

[b] In DMSO

TABLE II
Infrared frequencies[a] of anti-2-furan carboxaldoxime (β-FDH)[b] and its complexes (cm^{-1})

Assignments	β-FDH	[Co(FDH)$_4$Cl$_2$]	[Co(FD)$_2$]	[Cu(CH$_3$COO)$_2$(FDH)]$_2$	[Cu(FD)(OH)]$_2$	Cu(FDH)$_2$Cl	AgNO$_3$·2FDH
O–H stretching	3160b 3040b	3250s	–	3410s	3520s 3440s	3180b	3160b 3040b
O–H deformation	1448w 1323s	1440m 1323s	– –	1450w 1320s	1440w 1331s	1438m 1313s	1440sh 1320m
> C=N-stretching	1640m	1650m	1657m	1660m	1655m	1640m	1637s
=N–OH stretching	970m	970m	967sh	986m	980sh	968s	967b
M–O stretching	–	662s 637vs 615sh	430w	670b 633s 450b	640sh 521b 460b	668m 640s	–

[a] vs = very strong, s = strong, m = medium, b = broad, sh = shoulder, w = weak, vw = very weak.

[b] Assignment of the various frequencies of anti-2-furan carboxaldoxime has been done as described earlier.[8]

TABLE III
Infrared frequencies of anti-2-furan caboxaldoxime (β-FDH) and its complexes (cm^{-1})

Assignments	β-FDH	[Co(FDH)$_4$Cl$_2$]	[Co(FD)$_2$]	[Cu(CH$_3$COO)$_2$(FDH)]$_2$	[Cu(FD)(OH)]$_2$	Cu(FDH)$_2$Cl	AgNO$_3$·2FDH
Ring stretching	1565w 1480s 1380s 895w	1560s 1477s 1377vs 898w	1588s 1474s 1382vs	1563s 1478vs 1383vs	1590m 1479vs 1380vs 886sh	1560m 1480s 1380vs 900w	1563m 1480vs 1378vs 892w
C–O–C stretching	1240vs	1240vs	1231s	1240s	1230s	1245s	1237vs
C–H in plane deformation	1190s 1149vs 1088vs	1190vs 1140vs 1084vs	1192vs 1146s 1080s	1191vs 1150vs 1187s	1184s 1149s 1085s	1190s 1150s 1090s	1186vs 1142vs 1083vs
Ring breathing	1020vs	1020vs	1011s	1020b	1020b	1027s	1013vs
C–H out of plane deformation	923w 880sh 820b 750s	930s 821s 750vs	920w 865m 823sh 745vs	926m 875vw, 855b 823w 746s	927sh 857s 820sh 739s	932m 885vw 830vs 749vs	919s 880sh 821b 750s
Other bands	590sh 576s 570sh 335vw	590sh 571s 335vw	571s	1610s 1425s 1272s 590sh 573vs	1270m 590sh 574vs	580b 370w	1340m 805w 572s

the presence of three unpaired electrons in Co(II) (high magnetic moment may be due to the very high orbital contributions since the $^4T_{1g}$ ground state is three-fold degenerate) and the complex could thus be octahedral provided that β–FDH acts as a monodentate ligand. The evidence for the denticity of the ligand has been obtained from the infrared spectrum of the complex. The broad bands for O–H stretching vibrations at 3160 and 3040 cm^{-1} in the ligand, are shifted to a strong peak at 3250 cm^{-1} in this complex. This implies that the hydrogen bonding has been partly weakened as a result of complexation. The additional bands present in the complex (these are absent in the ligand spectrum) in the region 670–630 cm^{-1} are likely to be due to the Co–O (oxime) stretching vibrations as similar additional band around 600 cm^{-1} has also been observed in $[Co(TDH)_2Cl_2]$ complex, (TDH = 2-thiphene aldoxime) and this has been attributed for the Co(II)–O(oxime) stretching vibrations.[18] Moreover in the complex $[Co(FDH)_4Cl_2]$, four FDH ligand molecules are present and the ligand FDH will therefore favour coordination through the oxime oxygen rather than furan oxygen as in the latter there will be an overcrowding and hence greater steric hinderance. The >C=N– stretching frequency in the ligand at 1640 cm^{-1} shifts to 1650 cm^{-1} in the complex which also indicated that –CH=N–OH part of the ligand is involved in coordination. The shift of >C=N– stretching frequency to a higher value may be explained on the basis of the decreased electron density on nitrogen atom[19] in the complexes. 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 atom. Co–Cl stretching vibrations in this complex could not be assigned as the ligand has a band in the usual metal-halogen sensitive region. Two possible geometrical isomers of this octahedral complex, $[Co(FDH)_2Cl_2]$, could then exist corresponding to the position of two chlorine atoms, being either cis or trans.

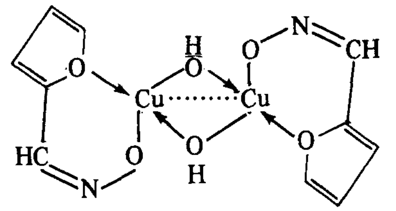
$[Co(FD)_2]$ The neutral complex, $[Co(FD)_2]$, containing the ionized ligand molecules is formed by the reaction of two moles of FDH with one mole of cobalt(II) acetate in an inert atmosphere. Conductivity measurements in nitrobenzene indicate its non-ionic nature and the magnetic moment of the solid (4.52 BM) suggests that the complex may be tetrahedral. The higher value of the magnetic moment than the spin-only value (3.89 BM), can be explained[20] on the basis that the spin-orbit coupling causes the $^4T_2$ state which is separated by Δ_t from the ground state to be mixed into the ground state, thus introducing orbital angular momentum, and making the actual magnetic moment, greater than the spin-only moment. The infra-red spectrum of this compound shows the absence of O–H stretching and deformation vibrational bands, and the >C=N– stretching frequency is observed at 1657 cm^{-1}. The furan modes also gets shifted considerably. The stretching vibrations of the Co–O bond is exhibited at 422 cm^{-1} in acetylacetonato cobalt(II) complexes[21] and at 491 and 412 cm^{-1} in cobalt(II) alkoxides.[22] Accordingly, a weak band at 430 cm^{-1} in the complex (II) is assigned to the Co–O stretching vibrations as this band is absent in the spectrum of the ligand. Hence it may be concluded that the complex $[Co(FD)_2]$ is tetrahedral with the two ionized FDH molecules acting as bidentate ligand, coordinating through furan and oxime oxygen atoms.

$[Cu(CH_3COO)_2(FDH)]_2$ The complex (III) is found to be neutral. The presence of acetate, is confirmed by the usual qualitative analysis and from its infrared spectrum, assignments of which have been made on the basis of earlier studies.[23-25] The free acetate ion shows two strong peaks at 1578 and 1425 cm^{-1} respectively corresponding to the CO_2^- antisymmetric and symmetric stretching vibrations. In the complex (III), these are present at 1610 and 1425 cm^{-1} respectively, while in the complex $[Cu(CH_3COO)_2 \cdot H_2O]_2$ these are at 1605 and 1425 cm^{-1} respectively. The NMR spectrum of this compound in pyridine gives a signal at 1.06 δ for the methyl protons of the acetato groups. A broad band at 450 cm^{-1} may be considered due to the Cu(II)–O (acetato) stretching vibrations as it is found at 455 and 465 cm^{-1} in copper(II) acetylacetonato[23] and alkoxide[24] complexes respectively. The broad band at 3160 cm^{-1} due to O–H stretching vibrations in the ligand gets shifted to a sharp peak at 3410 cm^{-1}, indicating the breaking up of the hydrogen bonding as a result of complexation. The >C=N– stretching frequency at 1640 cm^{-1} in the ligand gets shifted to 1660 cm^{-1} in this complex. The N–OH stretching frequency is considerably increased (by 16 cm^{-1}). Also there are additional bands in the region 670–630 cm^{-1} which can be attributed to Cu(II)–O (oxime) stretching vibrations, as these are absent in the ligand spectrum. The furan modes are not much affected. An alternate formula for this compound is $[Cu(CH_3COOH)_2(FD)]_2$ and the data that would distinguish this compound is the C–O–C stretching of furan which is observed at 1240 cm^{-1} in this ligand (Table III). If the Schiff base ligand is bidentate

then a shift to lower frequency will be observed in the complex. Since in this complex the band is not shifted, then the correct formula is $[Cu(CH_3COO)_2(FDH)]_2$ and it may thus be concluded that the ligand, FDH acts as monodentate and the bonding is likely to be through oxime oxygen. Molecular weight measurement in DMSO suggests it to be a dimer, and a very low magnetic moment indicates that there is an extensive quenching of the spin moment of the cupric ion due to the metal–metal interactions. Thus the structure appears to be similar to the one assigned to $Cu_2(OCOCH_3)_4 \cdot 2H_2O$,[26] with FDH occupying the position of water molecules, and the bonding of copper with FDH being through the oxime oxygen atom.

A similar series of compounds where two water molecules in $[Cu(OCOR)_2(H_2O)]_2$ are replaced by other ligands are also known, e.g., $[Cu(OCOCH_3)_2(am)]_2$[27] where am = py, α, β or γ-picoline; $[Cu(OCOC_6H_5)_2]_2$[28] where X = H_2O or py.

$[Cu(FD)(OH)]_2$ This copper(II) complex (IV) is neutral and is dimeric in solution as is indicated by the molecular weight determinations. It shows the presence of OH bridges in its infrared spectrum where sharp bands are obtained at 3520 and 3440 cm^{-1} corresponding to the O–H stretching vibrations. In the similar copper(II) complexes these vibrations are found in the region 3600–3400 cm^{-1} viz. in $[(am.py)_2Cu(OH)]_2(ClO_4)_2$[29] at 3590 cm^{-1} and in $[(X)Cu(OH)]_2Y_2 \cdot nH_2O$[30] at 3440 and 3550 cm^{-1} where X = bipy or phen; Y = Cl, Br or ClO_4; and n = 1, 2, 3 or 4. The O–H deformation bands and furan modes are also accordingly affected. A broad band at 460 cm^{-1} may be assigned to Cu(II)–O (furan) stretching vibrations on the similar basis as discussed for the complex (III). A broad band at 521 cm^{-1} may be assigned to Cu(II)–O(hydroxo) stretching mode as this is found at 590–543 cm^{-1} and 490 cm^{-1} in similar 2-amino pyridine[29] and bipyridine[30] complexes of Cu(II) respectively. The band due to Cu(II)–OH bending vibrations seems to have merged in the ring breathing vibrations, which is a very broad band at 1020 cm^{-1}. This has been found at 995 cm^{-1} in the similar bipyridyl complexes.[30] The magnetic moment of this complex is very low (0.28 BM) which is similar to the complex (III) and this compound is unaffected by ammonia, ethylenediamine and pyridine. Hence it may be concluded that the ligand acts here as bidentate while coordinating through both the oxygen atoms, and each copper atom is surrounded by four oxygen atoms, (two of FD^- and two of hydroxo bridges) forming a tetrahedron.



A number of similar copper(II) complexes of 2-pyridine carboxaldoxime (PDH), which is structurally similar to FDH are also known. These are of the type[31,32] $Cu_3(PD)_3(OH)X_2 \cdot nH_2O$ ($X^- = OH^-$, I^-, NO_3^-, ClO_4^-, $\frac{1}{2}SO_4^{2-}$). These also have anomalously low[32–34] magnetic moments, $\mu_{eff} \sim 1.0$ BM per copper(II) atom and the occurrence of a trinuclear Cu_3 core in which strong exchange interactions causes pairing of two of the three unpaired electrons associated with the three copper(II) atoms have been suggested.[34]

The possible reactions involved in the formation of the above complex (IV) can be put as follows:

$$\begin{tikzcd}
CuCl_2\cdot 2H_2O + 2FDH \arrow[r] & {[Cu(FDH)_2Cl_2]} + 2H_2O \\
\text{(in methanol) (in ethanol)} & \text{(red brown crystals)} \arrow[d, "\text{methanolic NaOAc}"] \\
{[Cu(FD)(OH)_2} \arrow[r, "+H_2O", "\text{hydrolysis}"'] & {[Cu(FD)_2]} \\
\text{(dark green precipitate)} & \text{(greenish brown solution) (unstable)}
\end{tikzcd}$$

The compound $[Cu(FDH)_2Cl_2]$ is already reported[7] and the complex (IV) can also be prepared from the above compound and is found to be identical. The intermediate compound $[Cu(FD)_2]$ could not be isolated as it was unstable.

$Cu(FDH)_2Cl$ This compound is diamagnetic suggesting the oxidation state of copper to be one (d^{10} system). Due to the high insolubility of this Cu(I) complex (V), the molecular weight and molar conductance could not be determined. However, in its infra-red spectrum it shows a broad band at 3180 cm^{-1} which indicates that the hydrogen bonding has not been broken up as a result of complexation and the ligand has a less chance to act as bidentate in this complex. Also there are additional bands in the region 670–630 cm^{-1} which can be attributed to the Cu(I)–O stretching vibrations while the >C=N– stretching frequency and the furan modes are not

much affected. There is a weak band at 370 cm^{-1} which may be due to Cu(I)–Cl stretching vibrations. The complex is likely to have a polymeric structure with the ligand FDH as monodentate.

$AgNO_3 \cdot 2FDH$ The silver(I) compound (VI) is diamagnetic and the molar conductance studies correspond to an ionic(1:1) compound. The suspension of this compound in water, gives a precipitate of AgCl with KCl solution, instantaneously. The adduct nature of this compound has also been established by passing its aq. alcoholic solution through a cation-exchanger where only the silver ions get absorbed. On passing the solution of this compound through an anion-exchanger, the solution was found to be free of nitrate ions. The ligand FDH is neither absorbed in a cation-exchanger nor in an anion-exchanger. In the infra-red spectrum of this compound, O–H stretching frequency is not at all affected while the >C=N– stretching frequency is observed at 1637 cm^{-1}. The furan vibrational modes are also not much affected. The presence of free nitrate is also shown in the infrared spectrum of this compound. Nitrate ion[35] is of D_{3h} symmetry and as a result of coordination the symmetry lowers to C_{2v}, which changes the vibrational spectrum of the free nitrate ion. Accordingly, besides the bands of the nitrate ion at 1400, 1052 and 720 cm^{-1}, the spectra of the complexes, have five new bands[35], 1540–1470, 1360–1315, 1040, 830–810 and 760–735 cm^{-1}. $AgNO_3$ shows peaks[35,36] at 1348 (vs) and 803 (w) cm^{-1} corresponding to the NO_3^- antisymmetric stretching and NO_3^- out of plane deformation vibrations respectively. These are present at 1340 (m) and 805 (w) cm^{-1} respectively in compound (VI), indicating that the NO_3^- part in this compound is not much different from the one in $AgNO_3$. Hence this silver compound (VI) may be considered just as an adduct.

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