

Studies on the Replacement Reactions in Some Metal Complexes Part—V : Ligand and Anion Replacement Reactions in Some Complexes of Nickel(II) Derived from Antifuran-2-carboxaldoxime

(Mrs.) P. R. SHUKLA and V. K. SINGH

Department of Chemistry, University of Lucknow, Lucknow-226 007

and

GOPAL NARAIN

Department of Chemistry, University of Saugar, Saugar-470 004

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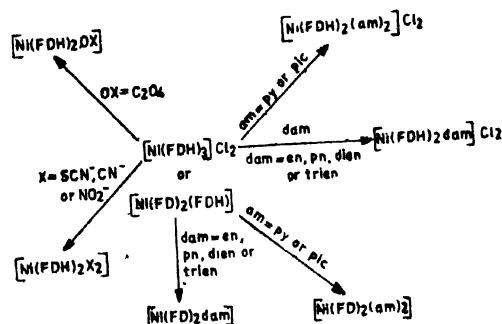
Some complexes of nickel(II) derived from the ligand antifuran-2-carboxaldoxime have been prepared and studied. Two types of parent complexes such as $[\text{Ni}(\text{FD})_2\text{FDH}]$ and $[\text{Ni}(\text{FDH})_3]\text{Cl}_2$, where FDH and FD refer to the neutral and anionic forms of the anti-oxime, have been prepared. A series of ligand replacement reactions on former, and both ligand and anion replacement reactions on latter, have been carried out and complexes of the type $[\text{Ni}(\text{FD})_2(\text{am})_2]$, $[\text{Ni}(\text{FD})_2\text{dam}]$, $[\text{Ni}(\text{FDH})(\text{am})_2]$ or $[\text{Ni}(\text{FDH})(\text{dam})_2]\text{Cl}_2$ and $[\text{Ni}(\text{FDH})_3(\text{X})_2]$ where am = pyridine (py), α -, β - or γ -picoline (pic), dam = ethylenediamine (en), propylene diamine (pn), 2,2'-bipyridyl (bipy), 1,10-phenanthroline (phen), diethylene triamine (dien) and triethylene tetramine (trien) and X = thiocyanate, cyanide and nitrite ions, have been obtained. All these have been assigned octahedral spin free structures on the basis of analytical, molar conductance, magnetic moment, infrared and electronic spectral data.

A survey of literature indicates that a large amount of work has been done on the transition metal complexes derived from various aldoximes, which act as potential ligands due to the presence of a number of donor sites in them. The use of heterocyclic oximes in which another donor is present *ortho* to the oxime group is expected to give more valuable information regarding the mode of bonding and stereochemistry of the oxime complexes¹⁻⁶. The compound antifuran-2-carboxaldoxime has, therefore, been used and in a previous communications its complexes with cobalt(II) were reported⁷. In the present paper the complexes of nickel(II) with the oxime in its neutral as well anionic forms are reported. By carrying out ligand and anion replacement reactions on these, many other mixed ligand complexes have been prepared which have been fully characterised by analytical, molar conductance, magnetic moment, infrared and electronic spectral data.

Experimental

The ligand antifuran-2-carboxaldoxime is prepared as described earlier⁷. The complex $[\text{Ni}(\text{FD})_2\text{FDH}]$ has been obtained by treating calculated amount of $\text{Ni}(\text{Ac})_2$ with the oxime and neutralising the solution with ammonia, while the complex $[\text{Ni}(\text{FDH})_3]\text{Cl}_2$ was prepared by treating nickel(II) chloride with three equivalents of oxime in methanol. A known weight of these was then suspended

in methanol and treated with the ammonium salt of the anion or the desired amine ligand in methanol. The resulting solution was refluxed for few hr, when a clear solution containing the new complex was obtained. The solid complexes were crystallized out from this solution by repeated treatments with petroleum ether. It was, however, found that in case of diethylenetriamine or triethylenetetramine the direct addition of the amines made the solution viscous and it was very difficult to crystallise out the complex from this. The stoichiometric quantity of amine was, therefore, dissolved in methanol and added dropwise with stirring. The various complexes so obtained are shown below.

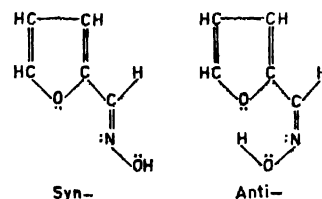


The molecular formulae of the complexes have been assigned by the estimation of percentages of

metal, C, H and N. The molar conductance has been measured in water or methanol and the data are listed in Table 1. The infrared spectra have been recorded on a infrared spectrometer model 221, while magnetic moments have been obtained by Gouy method. The electronic spectra were recorded in the range 200-2000 nm on a Cary 14 recording instrument in the form of nujal discs and are listed in Table 2.

Results and Discussion

The ligand furan-2-carboxaldoxime exists in the syn- and anti-forms as shown below.



These structures show that former can coordinate only through oxime nitrogen, but the latter through oxygen also. The oxime can also form complexes in the neutral as well as ionized state and both such

TABLE 1—ANALYTICAL, MOLAR CONDUCTANCE AND MAGNETIC DATA

Complex No.	Formulae	Analysis % , Found (Calcd.)					λ_{mhos}	μ_{eff} B.M.
		Ni	O	H	N	Cl		
1.	[Ni(FD) ₂ (FDH)]	16.25 (15.05)	46.32 (46.19)	8.28 (9.959)	10.56 (10.77)	—	2.40	2.94
2.	[Ni(FD) ₂ (py) ₂]	13.81 (19.48)	54.83 (54.95)	4.28 (4.15)	12.03 (12.81)	—	2.01	2.92
3.	[Ni(FD) ₂ (α -pic) ₂]	12.82 (12.62)	56.72 (56.80)	4.63 (4.767)	11.96 (12.04)	—	4.59	3.05
4.	[Ni(FD) ₂ (β -pic) ₂]	13.23 (12.62)	56.90 (56.80)	4.79 (4.76)	11.99 (12.04)	—	5.65	2.07
5.	[Ni(FD) ₂ (γ -pic) ₂]	12.78 (12.62)	56.77 (56.80)	4.70 (4.76)	12.10 (12.04)	—	3.04	2.99
6.	[Ni(FD) ₂ (en)]·2H ₂ O	16.44 (15.65)	39.01 (38.43)	4.99 (5.37)	14.38 (14.94)	—	—	3.49
7.	[Ni(FD) ₂ (pn)]·2H ₂ O	15.21 (15.09)	40.22 (40.13)	5.61 (5.69)	14.48 (14.40)	—	3.24	3.20
8.	Ni(FD) ₂ (dien)·2H ₂ O	15.03 (14.04)	40.16 (40.21)	5.98 (6.02)	16.69 (16.75)	—	—	3.05
9.	Ni(FD) ₂ (trien)·2H ₂ O	13.98 (12.78)	41.60 (41.67)	6.53 (6.557)	18.17 (18.22)	—	3.65	3.35
10.	Ni(FD) ₂ (bipy)·2H ₂ O	14.03 (12.46)	50.95 (50.98)	4.30 (4.27)	11.83 (11.89)	—	2.73	3.16
11.	[Ni(FD) ₂ (phen)]·2H ₂ O	11.76 (11.85)	53.23 (53.66)	4.11 (4.07)	11.33 (11.31)	—	—	3.13
12.	[Ni(FDH) ₂ Cl ₂]	11.67 (12.68)	38.88 (38.91)	3.22 (3.26)	8.99 (9.07)	13.56 (15.81)	127.31	3.251
13.	[Ni(FDH) ₂ (py) ₂ Cl ₂ ·2H ₂ O]	11.24 (10.75)	48.90 (48.90)	4.30 (4.48)	10.19 (10.26)	14.71 (12.98)	123.11	2.93
14.	[Ni(FDH) ₂ (en)Cl ₂ ·2H ₂ O]	12.11 (18.10)	32.19 (32.17)	4.87 (4.95)	12.58 (12.50)	15.23 (15.89)	—	3.17
15.	[Ni(FDH) ₂ (pn)Cl ₂ ·2H ₂ O]	11.82 (12.12)	38.71 (38.79)	5.28 (5.28)	12.19 (12.12)	18.78 (15.84)	183.71	3.17
16.	[Ni(FDH) ₂ (dien)Cl ₂ ·2H ₂ O]	13.26 (11.95)	34.80 (34.34)	5.49 (5.54)	14.20 (14.26)	15.83 (14.44)	115.71	3.06
17.	[Ni(FDH) ₂ (trien)Cl ₂ ·2H ₂ O]	11.76 (10.99)	35.89 (35.98)	6.12 (6.08)	15.79 (15.78)	11.19 (18.27)	135.81	3.049
18.	[Ni(FDH) ₂ (dipy)Cl ₂ ·2H ₂ O]	10.17 (10.79)	43.98 (44.15)	4.05 (4.07)	10.18 (10.29)	15.21 (13.03)	135.81	3.049
19.	[Ni(FDH) ₂ (phen)]·2H ₂ O	11.08 (10.33)	46.49 (46.51)	3.94 (3.90)	9.91 (9.86)	13.43 (12.48)	—	3.40
20.	[Ni(FDH) ₂ (SCN) ₂ ·4H ₂ O]	13.23 (12.51)	30.68 (30.72)	3.81 (3.86)	11.89 (11.94)	—	4.03	2.99
21.	[Ni(FDH) ₂ (NO ₂) ₂ ·4H ₂ O]	13.40 (13.19)	26.90 (26.99)	4.10 (4.07)	12.60 (12.59)	—	2.85	3.33
22.	[Ni(FDH) ₂ C ₂ O ₄]	17.32 (15.91)	39.12 (39.06)	2.76 (2.78)	7.52 (7.59)	—	2.04	3.34
23.	[Ni(FDH) ₂ (CN) ₂]	13.11 (17.63)	43.23 (43.28)	3.04 (3.02)	16.86 (16.92)	—	2.65	3.10

TABLE 2—ELECTRONIC SPECTRAL DATA

Complex No.	ν_1 (Obs.) kK	ν_2 (Obs.) kK	ν_3 (Obs.) kK	Dq(Obs.) cm^{-1}	B cm^{-1}	Dq(Calcd.) cm^{-1}	ν_1 (Calcd.) kK	ν_2 (Calcd.) kK	β
1.	9.09	15.15 14.09	28.57 25.65	909	914	916.2	16.37	27.90	0.903
2.	10.31	15.38 14.19	25.97	1031	923.8	965	16.28	27.86	0.913
3.	10.52	16.61 14.18	26.90	1052	1040	1020	18.95	29.63	1.02
4.	10.64	16.26 13.80	27.72 24.40	1064	1017	998.40	19.16	29.77	1.00
5.	10.33	16.13 13.93	27.02	1033	1009	998.2	18.60	29.01	0.999
6.	11.51	17.86 16.26	28.74 24.40	1087	1066	1159	20.70	30.80	1.02
7.	10.99	19.04 16.34	28.17	1099	1190	1066	19.80	30.20	1.17
8.	11.36	18.35 16.45	26.31 26.69	1093	1148	1124	20.46	30.64	0.882
9.	11.24	19.40 16.95	29.42	1124	1137	1115	20.23	30.49	1.00
10.	11.36	18.34 17.14	27.77	1186	1128	1105	20.45	30.63	1.01
11.	12.35	19.01 15.15	28.56 25.64	1184	1068	1046	20.37	30.61	1.02
12.	10.63	16.03 14.60	27.79	1063	957	926.2	17.23	28.50	0.945
13.	10.88	16.00	26.70	1088	999	989	17.64	28.75	—
14.	11.09	18.52 14.81	29.41 25.65	1109	1153	1134	19.95	30.30	0.874
15.	11.50	18.17 15.15	27.65	1150	1042	1020	20.67	30.80	1.01
16.	11.42	19.05 16.95	25.96	1142	1125	1108	20.54	30.70	0.900
17.	11.21	19.25 16.66	26.02	1121	1130	1097.4	20.17	30.45	0.98
18.	10.97	17.86 16.45	26.31	1097	1071	1050	19.73	30.16	0.944
19.	10.78	18.12 15.89	28.57 25.64	1078	1132	1110	19.40	29.93	1.12
20.	10.26	16.04	25.51	1026	1001	981	18.47	29.31	0.989
21.	9.803	15.80 13.57	26.45	980.3	984.2	964.6	17.65	28.75	0.972
22.	9.634	18.52 16.61	25.51 24.51	963.4	1102	1077	17.35	28.56	1.08
23.	10.73	17.86 15.15	28.75 25.64	1073	1116	1094	19.32	29.87	1.103

complexes of the antioxime have been prepared in the present study.

In the complex $[\text{Ni}(\text{FD})_2(\text{FDH})]$, two uninegative oxime ions and one neutral oxime group is attached to nickel(II), while in the complex $[\text{Ni}(\text{FDH})_3]\text{Cl}_2$, only three neutral oximes are attached and the charge of nickel(II) is neutralised by two chloride ions. These formulae are supported by the conductivity data of the complexes (Table 1). The above chart shows that in the former complex only ligand replacement reactions but in latter both ligand and anion replacement reactions have been possible and the formulae of the products so obtained have also been assigned on the basis of analytical and conductance data. The evidence for the coordination of ligands and the existence of oxime in the anti form is obtained by the infrared data, as discussed below.

In the ir spectra of free ligand [antifuran-2-carboxaldoxime] two bands appear at 3160 and

3040 cm^{-1} which are assigned to the intramolecularly bonded $-\text{OH}$ group as reported for other similar complexes. In the complexes no. 1 and 14-23, which contain neutral FDH, both these merge together and either one or two peaks appear at 3360 and 3280 cm^{-1} showing that the hydrogen bonding has broken down as a result of coordination. In the complexes no. 2-13 only ionized oxime ions are coordinated in which the $-\text{OH}$ group has been deprotonated and hence peaks in this region are absent^{8,9}. No band is seen in the spectra of free ligand below 600 cm^{-1} , while two distinct bands appear in all the complexes at 670 cm^{-1} and 510 cm^{-1} which are assigned to $\text{M}-\text{O}$ (oxime) and $\text{M}-\text{O}$ (furan ring stretches), respectively. The oxime appears to be bidentate in nature coordinating through oxime oxygen and furan ring oxygen¹⁰⁻¹². One very important consequence of the coordination of oxime oxygen is an increase in the electron density of the

nitrogen atom of the >C=N- group, which shifts by 20 cm^{-1} of that of free ligand (1640 cm^{-1}) and is observed in all the complexes at 1660 cm^{-1} ^{18,16}. The coordination through oxygen is probably favoured from the above structures according to which the stereochemical arrangement of bond and lone pair of electrons around nitrogen is such that it is somewhat hindered from approaching the metal ion. The coordination of other ligands is also indicated by the shifts in the position of the relevant infrared bands¹⁸⁻²⁰.

The μ_{eff} values of the complexes fall in the range 2.92-3.49 B.M. (Table 2) indicating octahedral high spin structures. The same structure is confirmed by the electronic spectra where three characteristic transitions ν_1 , ν_2 and ν_3 are seen at 11.00, 16.50 and 25.00 kK, respectively. The weak band at 13.50 kK in some complexes is assigned to the spin forbidden transition ${}^3A_{2g}(\text{F}) \rightarrow {}^1E_g(\text{D})$ which becomes partially allowed in these complexes due to the lowering of symmetry as different groups are present in the coordination sphere^{20,21}. The values of Dq, B and β have been calculated (Table 2) and these justify the assignment of octahedral structure to complexes²²⁻²⁴.

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