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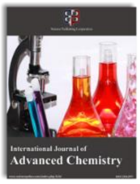

Some complexes of N-aryl furfural nitrones with Co (II), Ni (II), Cu (II), Zn (II) and Cd (II) chlorides

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Abstract

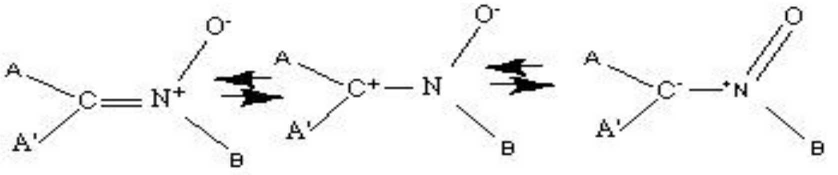
Some new metal(II) dichloride complexes with the ligands substituted nitrones of the general formula [ML_2Cl_2], where M= Co(II), Ni(II), Cu(II), Zn(II) and Cd(II), L=$OCH=CHCH=C-CH=N(O)C_6H_4X$ (X=H,p-CH_3,CH_3O,CH_3CO,F,Cl,and Br) have been prepared and characterized by elemental analysis, IR,^1H,^{13}C NMR and Vis/Uv spectroscopy. The IR spectral data showed that the nitrone ligands coordinated with the metal ion through the most active atom of the N-oxide to give square planner coordinate (Cu,Ni,) complexes and (Zn,Cd,Co) tetrahedral complexes. No correlation was observed between the N-O vibrations stretching high frequency ν (N-O) of the complexes and the Hammet (σ) constants.

Keywords: *Furfural; Hammet Constants; Metal Complex; Nitrones.*

1. Introduction

Preparation of nitrone compounds and its derivatives had much attention because of the biological importance, new methods of prepared nitrone compounds have much attention (David et.al, Novikov et.al). Some of these methods have been applied to the preparation of complexes molecules with useful biological activity such as antibiotics and glycosides inhibitors (Guo & Sadler 1999, Guo & Sadler 1999,Gothelf &.Jorgenson 1999, Allaf et.al 1996, Charmier et.al 2003, Saxena & Huber 1989). Therefore, new methods of activation, such as microwave chemistry and coordination to a metal center, have been attempted. In fact, it was observed that the microwave field decreased the activation energy of various types of reactions in particular with organonitrones(Caddick 1995). Moreover, metals in coordination processes can dramatically increase the reactivity of organonitriles (Yu &. Pombeiro, 2002, Michelin et.al. 1996) and metal-mediated processes can lead to the formation of heterocyclic species Yu &. Pombeiro, 2002).

Nitrones have been recognized as having the following resonance structure



When A, A` or B is a mesmeric substituent the nitrone group (-C=NO-) will, of course, interact mesomerrically with the substituent and thereby will probably exert an electron-attracting effect on the latter.

The ^{13}CNMR and ^{1}H1NMR study showed (Taqa et.al.1993), when a strong electron-donating group is in the Para position of a phenyl ring the nitrone acted as an electron-withdrawing group. For strong electron-withdrawing substituent the nitrone group acted as an electron donor. Thus they concluded that the nitrone group behaved as an electron-withdrawing or donating

In the current work, we have presented the reaction between metal chloride Co (II), Ni (II), Cu (II), Zn (II), Cd (II) and N-arylfurfuralnitrones(fig1) in order to examine the type of interaction between metals and this type of ligands as they contain more than a possible donor site. Also measure the effect of substituentuent on the mechanism formation of complexes using Hammet equation. To the best of our knowledge, this work is a novel.

2. Experimental

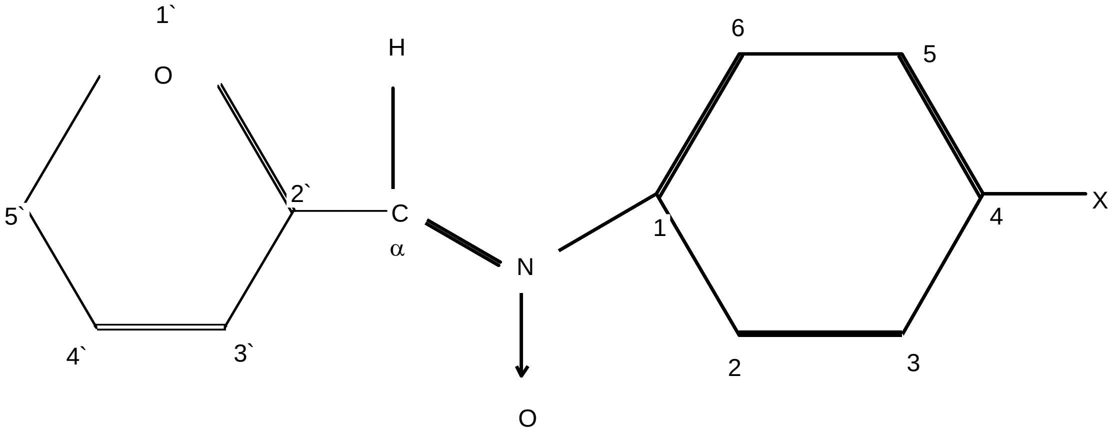
The ligands p-x-phenyl-N-furfural nitrones (X=H, Cl, Br, F, OH, CH_3, OCH_3 and $COCH_3$) were prepared as described previously with substituted X-C_4H_4NHOH in ethanol (Arumuga et.al. 1984). The free nitrone ligands were purified by crystallization.

Preparation of complexes: The following standard method was used; molar quantities (usually 1:2 mmole) of metal salts and the nitrone ligand (L) were dissolved in absolute ethanol (25ml) at ambient temperature. The colored solution and the complex started to deposit. The formed precipitate was filtered, washed several times with small portions of ether and dried. The yield is almost quantitative.

Metal analysis of some of the complexes was determined, Nickel metal was determined as dimethylglyoxime complexes (Vogel 1972). Cobalt, zinc, copper and cadmium metals were determined by the pyridine method (Vogel 1972).

^{13}C and ^{1}H1NMR spectra were recorded at 25°C on a Bruker DPX 300MHz spectrometer at the department of Chemistry, College of Science, Jordan.

IR spectra were recorded on an Infrared spectrophotometer BRUKER (TENSOR 27), conductivity measurements were done for 10^{-3}M solutions of the complexes in ethanol and dimethylforamide at room temperature (25°C), using a Jenway conductivity meter model 4070. Visible spectra were recorded Ultraviolet–Visible spectrophotometer (UV -1650 PC).



L

L$_1$: X=H
L$_2$: X=CH_3
L$_3$: X=OCH_3
L$_4$: X=$COCH_3$
L$_5$: X=F
L$_6$: X=Cl
L$_7$: X=Br

Fig. 1: The Nitrones Ligands Used in the Coordination with Mcl_2 (M= Mn, Co, Ni, Cu, Zn and Cd).

3. Results and discussion

The IR data in Table I confirmed the formation of the complexes. There are changes in the frequencies of the C=N band upon complexation, but especially significant is the appearance of a new band at ca. 340 cm^{-1}, attributed to υ(M-O), which served as a good indicator of coordination.(Allaf &Al-Tayy 1990). Moreover, the drastic shift in the υ (N-O) frequency is clear evidence for the interaction between the NO group of the nitrone ligand and metal. However, coordinatid lead to a shift to lower frequency and the values of ν (NO) $_{\text{complex}}$- ν (NO)$_{\text{ligand}}$ showed a systematic variations from 15-to-50 cm^{-1} (Table1), and this may be attributed to a decrease in the NO group upon coordination(A l-Allaf et.al 1994). On the other hand the ν (C=N) frequency of the ligand show a great change to a higher values upon coordination and the values of ν (CN)$_{\text{complex}}$- ν (CN)$_{\text{ligand}}$ show again systematic variations from 25 to 45cm^{-1}. This may be due to the increase in the bond order between C and N upon coordination. In contrast, the ν (C-O) frequency of the ligand which appeared in the range(Silverstein et.al 1974) 1070-1090cm^{-1} remains almost constant upon coordination supported that the furfural oxygen remained unchanged upon coordination supported that the furfural oxygen is not involved in the coordination.

3.1. Molar conductivities

Molar conductivities for 10^{-3}M solutions of the complexes in two different solvents, ethanol and DMF, at ambient temperature 25˚C were in the range 1.3-11.82 and 0.05-10.2 ohm cm^2 $mole^{-1}$ respectively,(Table II) suggesting the present of non-conductive species(Kettle 1975)(i.e., non-ionic) complexes in the solvents used.

3.2. NMR spectra

The magnetic resonance (Table III) showed shifted α-H of ligand to complex in d_6DMSO solvent and this confirms coordination. The ^{13}C NMR spectral data were recorded to provide an additional indicator for the coordination number. In (Table IV), shows a clear change in the chemical shifts of the carbon atoms of the organic nucleus, especially significant are those of C-α, C-1, C2□`,C3`and C5`(Fig1). Carbon atoms were assigned by comparison with other related organic compounds as model compounds (Levy et.al 1980). The carbon C-α showed a downfield shift on going from the free ligand to its complex (ca.1.5ppm) and this clearly suggested that the C=N bond order is increased due to complexiation. This is supported by the stretching frequency of the C=N bond which shifted to a higher value on complexation. Similarly, C-1 is also affected upon coordination and is shifted upfield by ca. 1ppm. Although the furfural nucleus had not been involved in the coordination, nevertheless, the peak for C-2` is shifted upfield whereas those of C-3` and C-5` are shifted downfield upon coordination. We believe that this may be due to the inductive effect caused by coordination. This in turn causes a great drainage of electron density from the furfural oxygen, through conjugation to C2`, then to C-α and so on.

Table I: Physical Properties and Infrared Spectra for Complexes

Complex	Color	Empirical Formula	Formula Weight	Yield (%)	mp˚C	ν(N-O)	ν (C=N)	ν (M-O)	ν (M-Cl)
$CoCl_2.L_1$	D.red	$C_{22}H_{18}\ O_4N_2CoCl_2$	504.23	90	>350	1260m	1625m	335w	250s
$NiCl_2.L_1$	red	$C_{22}H_{18}\ O_4N_2NiCl_2$	503.995	90	>350	1270s	1620m	350m	260m
$CuCl_2.L_1$	green	$C_{22}H_{18}\ O_4N_2CuCl_2$	508.847	90	d306	1260m	1620m	350m	260s
$ZnCl_2.L_1$	white	$C_{22}H_{18}\ O_4N_2ZnCl_2$	510.691	90	>350	1265m	1610m	345w	260m
$CdCl_2.L_1$	whit	$C_{22}H_{18}\ O_4N_2CdCl_2$	557.712	90	>350	1270s	1610m	340w	265m
$CoCl_2.L_2$	red	$C_{24}H_{22}O_4N_2CoCl_2$	532.288	85	290d	1270s	1610m	350m	270s
$NiCl_2.L_2$	Brown	$C_{24}H_{22}O_4N_2NiCl_2$	532.049	95	>350	1270s	1620m	350m	260m
$CuCl_2.L_2$	green	$C_{24}H_{22}O_4N_2CuCl_2$	536.901	90	290d	1265m	1620m	340w	235w
$ZnCl_2.L_2$	light white	$C_{24}H_{22}O_4N_2ZnCl_2$	538.745	90	310d	1260m	1625m	340w	255w
$CdCl_2.L_2$	white	$C_{24}H_{22}O_4N_2CdCl_2$	585.766	94	266d	1270s	1620m	335w	245w
$CoCl_2.L_3$	red	$C_{24}H_{22}O_6N_2CoCl_2$	564.287	40	>350	1275m	1625m	350w	250s
$NiCl_2.L_3$	red	$C_{24}H_{22}O_6N_2NiCl_2$	564.047	90	>350	1260s	1628m	350m	250m
$CuCl_2.L_3$	green	$C_{24}H_{22}O_6N_2CuCl_2$	568.9	70	189d	1270m	1615m	335w	270s
$ZnCl_2.L_3$	white	$C_{24}H_{22}O_6N_2ZnCl_2$	570.744	65	>350	1270s	1625m	340w	243w
$CdCl_2.L_3$	white	$C_{24}H_{22}O_6N_2CdCl_2$	617.765	86	>350	1265m	1630m	340w	235w
$CoCl_2.L_4$	red	$C_{26}H_{22}O_6N_2CoCl_2$	588.309	85	247	1270s	1615m	340w	255s
$NiCl_2.L_4$	red	$C_{26}H_{22}O_6N_2NiCl_2$	588.069	90	>350	1270s	1610m	355w	250m
$CuCl_2.L_4$	Dark green	$C_{26}H_{22}O_6N_2CuCl_2$	592.922	88	300d	1280b	1610m	355w	265s
$ZnCl_2.L_4$	white	$C_{26}H_{22}O_6N_2ZnCl_2$	594.766	69	278-290d	1270m	1620m	335m	250s
$CdCl_2.L_4$	white	$C_{26}H_{22}O_6N_2CdCl_2$	641.787	89	350d	1275s	1625m	350w	250s
$CoCl_2.L_5$	Pale red	$C_{22}H_{16}\ O_4N_2CoCl_2F_2$	540.216	96	>350	1270s	1620m	340w	270m
$NiCl_2.L_5$	Red	$C_{22}H_{16}\ O_4N_2NiCl_2\ F_2$	539.976	90	>350	1265s	1620m	340w	270m
$CuCl_2.L_5$	Green	$C_{22}H_{16}\ O_4N_2CuCl_2\ F_2$	544.828	90	310d	1270s	1615m	340w	270m
$ZnCl_2.L_5$	White	$C_{22}H_{16}\ O_4N_2ZnCl_2\ F_2$	546.672	78	289d	1270m	1620m	350w	270m
$CdCl_2.L_5$	White	$C_{22}H_{16}\ O_4N_2CdCl_2\ F_2$	593.693	68	218d	1265m	1625m	350w	255s
$CoCl_2.L_6$	Red	$C_{22}H_{16}\ O_4N_2CoCl_4$	573.124	80	290	1265m	1610m	355w	255w
$NiCl_2.L_6$	Red	$C_{22}H_{16}\ O_4N_2NiCl_4$	572.884	90	317	1265m	1615m	355w	255w
$CuCl_2.L_6$	Green	$C_{22}H_{16}\ O_4N_2CuCl_4$	577.737	79	289	1265m	1620m	355m	255w
$ZnCl_2.L_6$	White	$C_{22}H_{16}\ O_4N_2ZnCl_4$	579.581	95	>350	1260m	1620m	340m	240s
$CdCl_2.L_6$	white	$C_{22}H_{16}\ O_4N_2CdCl_4$	626.602	89	353d	1260m	1620m	340m	270w
$CoCl_2.L_7$	Red	$C_{22}H_{16}\ O_4N_2CoCl_2Br_2$	662.027	68	216	1265m	1620m	355w	270w
$NiCl_2.L_7$	Red	$C_{22}H_{16}\ O_4N_2NiCl_2\ Br_2$	661.787	70	327d	1265m	1620m	355w	255s
$CuCl_2.L_7$	Pale green	$C_{22}H_{16}\ O_4N_2CuCl_2\ Br_2$	666.64	87	>350	1265m	1610m	355w	270w
$ZnCl_2.L_7$	White	$C_{22}H_{16}\ O_4N_2ZnCl_2\ Br_2$	668.484	78	268	1270s	1610m	355w	270w
$CdCl_2.L_7$	White	$C_{22}H_{16}\ O_4N_2CdCl_2\ Br_2$	715.505	96	219	1270s	1615m	355w	270w

D: decompose, m: medium, s: strong, w: weak

Table II: HCN, Metal Analysis and Conductivity Value for the Complexes.

Complex	H	C	N	Metal %	Conductivity in DMF	Conductivity in ethanol
$CoCl_2.L_1$	3.598(3.55)	52.404 (52.50)	5.555(5.71)	11.687(11.91)	4.92	5.33
$NiCl_2.L_1$	3.599(3.61)	52.429(52.399)	5.558(5.62)	11.645(11.8)	8.30	6.16
$CuCl_2.L_1$	3.565(3.67)	51.929(52.21)	5.505(6.01)	12.48(12.22)	4.44	1.56
$ZnCl_2.L_1$	3.552(3.59)	51.742(51.98)	5.485(5.66)	12.08(12.35)	5.67	5.99
$CdCl_2.L_1$	3.253(3.19)	47.379(47.16)	5.022(5.15)	20.155(20.21)	2.38	8.21
$CoCl_2.L_2$	4.165(3.99)	54.155(54.21)	5.262(5.41)	11.071(11.21)	0.05	6.34
$NiCl_2.L_2$	4.167(4.16)	54.180(54.20)	5.265(5.26)	11.031(10.99)	10.2	6.16
$CuCl_2.L_2$	4.130(4.16)	53.690(53.72)	5.217(5.21)	11.835(11.770	10.02	4.70
$ZnCl_2.L_2$	4.115(4.11)	53.506(53.62)	5.199(5. 23)	12.137(11.98)	4.23	6.44
$CdCl_2.L_2$	3.785(3.77)	49.211(50.01)	4.782(7.77)	19.190(20.32)	5.30	1.30
$CoCl_2.L_3$	3.745(3.77)	48.687(48.75)	4.731(4.57)	10.443(11.00)	5.5	4.99
$NiCl_2.L_3$	3.931(3.66)	51.106(51.00)	4.966(5.02)	10.4057(10.41)	6.01	9.00
$CuCl_2.L_3$	3.897(4.01)	50.670(51.01)	4.924(4.89)	11.1699(11.32)	0.09	6.99
$ZnCl_2.L_3$	3.38(3.16)	50.50(50.12)	4.90(4.99)	11.45(11.55)	6.12	3.21
$CdCl_2.L_3$	3.589(3.47)	46.662(46.81)	4.534(4.64)	18.196(18.65)	5.09	3.67
$CoCl_2.L_4$	3.769(3.80)	53.081(53.22)	4.761(4.75)	10.017(9.93)	8.77	2.78
$NiCl_2.L_4$	3.770(3.79)	53.103(53.15)	4.763(4.81)	9.9806(10.24)	8.77	3.56
$CuCl_2.L_4$	3.739(3.69)	52.668(52.69)	4.724(4.75)	10.717(11.01)	9.04	7.66
$ZnCl_2.L_4$	3.728(3.76)	52.505(52.49)	4.710(4.71)	10.994(10.68)	9.91	6.90
$CdCl_2.L_4$	3.455(3.47)	48.658(48.69)	4.364(4.33)	17.5153(17.58)	2.56	2.78
$CoCl_2.L_5$	2.985(3.01)	48.914(49.11)	5.1856(5.21)	10.909(11.23)	10.0	4.98
$NiCl_2.L_5$	2.986(3.12)	48.935(49.04)	5.187(5.22)	10.869(11.05)	8.99	9.65
$CuCl_2.L_5$	2.960(2.78)	48.500(48.48)	5.141(5.19)	11.6634(11.31)	6.78	7.98
$ZnCl_2.L_5$	2.950(3.10)	48.336(48.54)	5.124(5.12)	11.96(12.11)	9.45	4.93
$CdCl_2.L_5$	2.716(2.69)	44.508(45.00)	4.718(4.73)	18.934(19.09)	7.99	5.91
$CoCl_2.L_6$	2.813(2.82)	46.105(46.23)	4.887(4.87)	10.287(10.51)	3.33	2.56
$NiCl_2.L_6$	2.815(2.79)	46.124(46.21)	4.889(4.90)	10.245(10.00)	3.56	3.89
$CuCl_2.L_6$	2.791(2.79)	45.737(45.77)	4.848(4.84)	10.99(11.43)	6.98	3.878
$ZnCl_2.L_6$	2.782(2.67)	45.591(45.62)	4.833(4.84)	11.282(11.44)	3.99	5,98
$CdCl_2.L_6$	3.421(3.45)	48.185(48.24)	4.322(4.33)	17.939(18.31)	8.99	9.85
$CoCl_2.L_7$	2.43(2.60)	39.91(42.31)	4.23(4.48)	8.91(8.44)	5.78	6.66
$NiCl_2.L_7$	2.43(2.55)	39.92(41.77)	4.23(4.39)	8.86(8.89)	6.88	7.49
$CuCl_2.L_7$	2.41(2.83)	39.63(39.11)	4.20(4.78)	9.53(9.21)	3.99	4.98
$ZnCl_2.L_7$	2.41(2.82)	39.52(39.23)	4.19(4.91)	9.78(9.19)	8.99	8.90
$CdCl_2.L_7$	2.25(2.79)	36.93(36.69)	3.91(4.17)	15.71(15.21)	9.34	10.9

( ) found

Table III: Proton NMR Data, Δ (Ppm) and J (H_2), For Selected Free Ligands and Their Metal Complexes

Compound	δ X	δ H-C=N	δ H2,6	δ H3,5	δ H 3`	δ H4`	δ H5`
L^1	7.44m	8.12s	7.76m	7.44m	7.54d J=1.5	6.60dd J=1.6	7.98d J=3.5
$NiCl_2.L_1$	7.55m	8.12s	7.72m	7.50m	7.65d J=1.4	6.70dd J=1.6	8.00d J=3.6
L^2	2.4s	8.12s	7.68d J=8.4	7.25 d J=8.4	7.56 d J=1.2	6.63 dd J=1.5	7.99 d J=3.5
$CuCl_2.L_2$	2.39 s	8.05 s	7.57d d J=8.4	7.25 d J=8.1	7.60 d J=1.3	6.65 dd J=1.5	7.96 d J=3.6
L^3	3.81 s	8.05 s	7.70 d J=9.0	6.91 d J=9.0	7.53 b	6.60 dd J=1.5	7.93 d J=3.4
$CdCl_2.L_3$	3.88 s	8.06 s	7.71 d J=8.5	6.97 d J=9.0	7.63b	6.67 dd J=1.6	7.95 d J=3.6
L^4	2.60 s	8.25 s	8.09 d J=8.5	7.92 d J=8.7	7.62 d J=1.3	6.67 dd J=1.6	8.08 d J=3.0
$ZnCl_2.L_4$	2.65 s 8.12 s	8.23 s	8.08 d J=8.9	7.90 d J=8.6	7.64 d J=1.3	6.68 dd J=1.6	8.04 d J=3.6
L^6	------	8.14 s	7.75 d J=8.8	7.42 d J=8.8	7.57 d J=1.5	6.63 dd J=1.7	8.00 d J=3.5
$CoCl_2.L_6$		8.12s	7.69 d J=8.5	7.46 d J=8.5	7.66 d J=1.5	6.69 dd J=1.6	7.97 d J=30

a) Downfield from internal TMS at room temperature using $CDCl_3$ as a solvent. S, single;d,double;dd,doublet of doublets;m,multiple.
b) Poorly resolved doublet (broad).

Table IV: Carbon-13 NMR Data[a], Δ (Ppm) and J (H_2), For Selected Free Ligands and Their Metal Complexes.

Compound	δx[c]	δC-α	δ C-1	δC-2,6	δC-3,5	δ C-4	δC-2`	δC-3`	δC-4`	δC-5`
L^1	________	144.7	147.6	121.1	129.2	130.0	147.3	116.5	112.7	124.3
$CoCl_2.L_1$	-------	146.6	146.6	121.8	129.5	130.6	146.6	118.9	113.2	128.2
L^2	21.1	144.5	147.6	120.8	129.7	140.2	145.1	116.2	112.7	123.8
$CuCl_2.L_2$	21.2	146.0	146.6	121.6	129.9	141.0	144.2	118.8	113.2	127.9
L^3	55.6	144.4	140.6	114.1	123.5	160.7	147.7	116.1	112.7	123.8
$CuCl_2.L_3$	55.7	145.8	139.8	114.4	123.0	161.1	146.7	118.4	113.1	127.9
L^4	26.8	145.3	150.0	121.2	129.4	137.9	147.4	117.7	113.0	124.9
$ZnCl_2.L_4$	26.8	146.0	149.7	121.5	129.0	138.0	147.0	118.6	113.0	126.5
L^6	________	144.9	147.4	122.3	129.3	135.7	145.6	116.9	112.8	124.2
$NiCl_2.L_6$	-------	146.4	146.5	123.0	129.6	136.4	144.9	119.2	113.3	128.0

a) Downfield from internal TMS at room temperature using $CDCl_3$ as a solvent. S, single; d,double; dd,doublet of doublets;m,multiple.
b) Poorly resolved doublet (broad).

From Fig 1 It can be seen that only two active donor site, i.e., the furfural oxygen and the nitrone oxygen, participate in bonding. Whereas the ligands L3 and L4 contain further donor site, i.e., the methoxy oxygen and the acetoxy oxygen atoms, respectively. Nevertheless, the spectral data showed that both groups, the methoxy and the acetoxy, were not involved in the complexation with metal. Therefore, the only possible donor sites of all ligands are the furfural oxygen and the nitrone oxygen atoms, thus the nitrones can behave as bidentate ligands, since the furfural group can rotate freely around the C2-Cα bond, and both oxygens can be arranged in such a way that they can complex with metal in a bidentate fashion. However, this is not the case with complexes, in which the IR spectral data showed that all of these ligands coordinate with metal in a bidentate fashion via both oxygen atoms (A l-Allaf et.al 1994, Al-Allaf et.al.1990).

The electronic spectra of the copper (II) complexes showed a single broad and poorly defined asymmetric band around 17500 cm^{-1} and the spectra of nickel (II) Complexes showed a band around 20000cm^{-1}. These results were consistent with square-planar structures, since the four lower orbitals are often so close together in energy, that individual transitions therefrom to the upper d level cannot be distinguished – hence the single absorption band(Lever1984).

The nickel (II) complexes showed a diamagnetic behavior consistent with square-planar environment around the metal ion. Magnetic susceptibilities of the copper (II) complexes were 1.87 BM. The effective magnetic moments were in accordance with diluted monomeric units (Carl& Magnetochemistry1986, Nicholls 1974).

From these data, square-planar structures may be proposed for the nickel (II) and copper (II) complexes with the monodentate ligand and the fourth coordination position occupied by two chloride ions, as depicted in fig.2; A similar structure but tetrahedral may be suggested for the zinc (II) and cadmium (II) complexes.

Studies of the magnetic and spectral properties of the prepared Co (II) complexes gave μ_{eff} values (3.59-3.7 BM) and one electronic spectral band in the visible spectrum at (14850, 16100 cm^{-1}) which assignment to $^4A_2$ ------→ $^4T_{1\ (p)}$. The magnetic moment of cobalt (II) indicates the presence of three unpaired electrons. These values suggest the geometry of tetrahedral configuration. The suggestion were confirmed by a band in electronic spectra which is assigned to ($^4A_2$ -------→ $^4T_{1\ (P)}$) transition (Honnick & Zuckerman 1978).

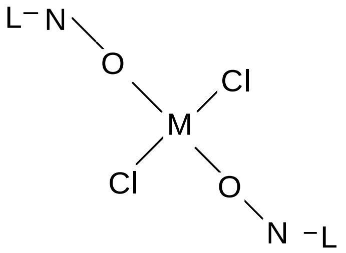


Fig. 2: The Suggested Structure for the $Mcl_2.L_2$ Complexes (For M and L See Fig. 1).

No correlation were observed between the N-O vibration stretching frequency ν (N-O) of the complexes with the Hammet (σ) constants (Fig.3) i.e. the plot of ν (N-O) for a given measurements with sigma constant of Para substituent constant (Hansh & Taft 1991) will not give a straight line, it is likely that the mechanism of the formation of complexes changed upon adding a different substitute. Other deviations from linearity may be due to a change in the position of the transition state. In such a situation, a certain substitute may be caused the transition state to appear earlier (or later) in the reaction mechanism (Anslyn & Doughert).

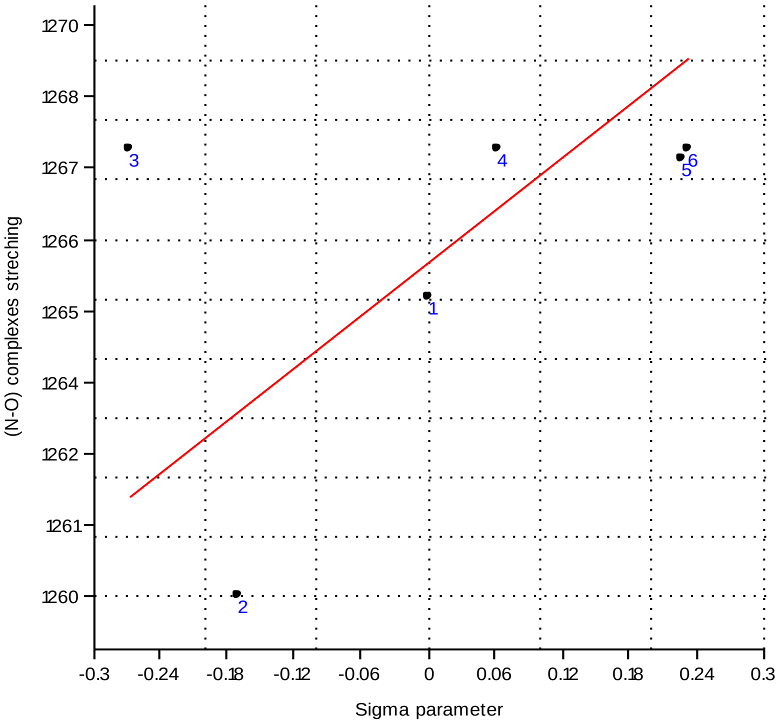


Fig. 3: The Correlation between the Nn-O of Complexes and Hammet Constant Σ.

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