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Synthesis and Characterization of Homobinuclear Complexes with 4-Substituted-2,6-diformylphenol Bis-aroylhydrazones

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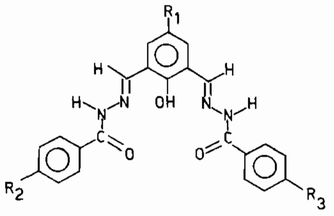
Multidentate ligands incorporating two metal ions are useful in studying the magnetic interactions between the metal ions; moreover they are interesting as models of metalloenzymes and in application to catalysis.

In the past few years a number of binucleating ligands [1] have been reported, containing either substituted diformyl phenols [1–3], or diformylthiophenols [1, 4]; heptantriones [5, 6] or 1,4-dihydrazinophalazines [7, 9], although a few other examples are known [10, 11].

Diformylthiophenols based on acylhydrazine side chains have been recently used successfully to produce palladium(II) binuclear complexes [12] with a good solubility in organic solvents. However, it has been recently reported [13] that in 2,6-diacetylpyridine-bis-aroyl-hydrazone uranyl complexes, the two hydrazonic protons show different pK_a, so that it is possible to selective deprotonate the complexes by using stoichiometric amounts of base.

We have synthesized ligands of the type I for studying the reactivity of homobinuclear complexes in the presence of variable amounts of base in order to test the possibility of obtaining, owing to the presence of acidic protons in the used ligands, several complexes in which the organic molecule acts from neutral up to trianionic ligand:



(I)

Ia $R_1 = CH_3$; $R_2 = R_3 = OCH_3$

Ib $R_1 = Cl$; $R_2 = R_3 = CH_3$

The ligands were prepared by reacting the 4-substituted diformylphenol, prepared as reported in

TABLE I. Analytical Data of Ligands and Complexes.

Ligands and Complexes	Calcd. %				Found %			
	C	H	N	Cl	C	H	N	Cl
Ia = H_3L	65.20	5.25	12.16	–	65.11	5.31	12.42	–
$LNi_2Cl \cdot 4H_2O$	43.99	4.25	8.21	5.21	44.18	4.10	8.53	5.36
$LCo_2Cl \cdot C_2H_5OH$	49.37	4.11	8.53	5.41	49.04	4.14	7.94	5.94
$LPd_2Cl \cdot DMF$	43.17	3.60	8.99	4.56	42.87	3.27	9.46	4.35
$LZn_2Cl \cdot C_2H_5OH$	48.41	4.03	8.37	5.30	48.19	4.37	7.81	4.87
$LCu_2Cl \cdot C_2H_5OH$	48.68	4.06	8.41	5.33	48.77	3.98	8.22	5.45
$L(VO)_2OC_2H_5$	50.96	4.09	8.81	–	51.30	4.16	8.65	–
$LNi_2(OH) \cdot H_2O$	49.23	3.94	9.19	–	49.20	4.19	8.73	–
Ib = H_3L'	64.21	4.71	12.47	7.89	64.37	4.55	12.30	7.91
$H_2L'Ni_2Cl_3 \cdot 4H_2O$	38.64	4.02	7.51	19.05	38.25	3.49	7.30	18.68
$HL'Ni_2Cl_2 \cdot 2H_2O$	42.93	3.43	8.35	15.87	42.87	3.37	7.93	15.23
$L'Ni_2Cl \cdot 2H_2O$	45.39	3.47	8.85	11.19	45.70	3.71	8.97	11.38
$L'Ni_2(OH) \cdot 2H_2O$	46.76	3.73	9.09	5.76	46.64	3.27	8.74	5.82

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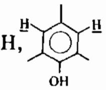
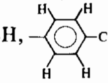
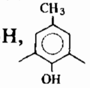
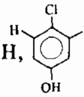
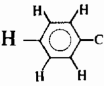
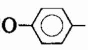
TABLE II. I.R. (cm^{-1}) and ^1H NMR Spectra of the Ligands and Complexes

Ligands and Complexes	ν(OH)	ν(NH)	ν Amide I	νC=N or C=N–N=C
Ia = H_3L	3372mb	3207, 3188m	1646s	1622sh
$LCu_2Cl{\cdot}C_2H_5OH$	3430m			1626sh
$LPd_2Cl{\cdot}DMF$			1670ms (DMF)	1610s
$LCo_2Cl{\cdot}C_2H_5OH$	3420m			1611s
$LZn_2Cl{\cdot}C_2H_5OH$	3438m			1623sh
$L(VO)_2OC_2H_5$				1615sh
$LNi_2Cl{\cdot}4H_2O$	3430s			1615s
$LNi_2(OH){\cdot}H_2O$	3434s			1613s
Ib = H_3L'	3439msb	3269, 3237b	1651s	1620sh
$H_2L'Ni_2Cl_3{\cdot}4H_2O$	3414msb 3386b	3269b, 3166b	1634ms	1540s
$HL'Ni_2Cl_2{\cdot}2H_2O$	3436msb 3331b	3189mb	1637sh	1614s 1543sh
$L'Ni_2ClJ2H_2O$	3430m			1615s
$L'Ni_2(OH){\cdot}2H_2O$	3422sb			1617s

The ^1H n.m.r. (DMSO-d_6) of Ia shows· δ 12 17 (s, 1H, *OH*), δ 11.88 (s, 2H, *NH*); δ 8.69 (s, 2H, $=\overset{H}{C}\langle$), δ 7.52 (s, 2H, ), δ 7.46 (q, AA'BB', 8H, ) δ 3.84 (s, 6H, $-OCH_3$), δ 2.31 (s, 3H, ).

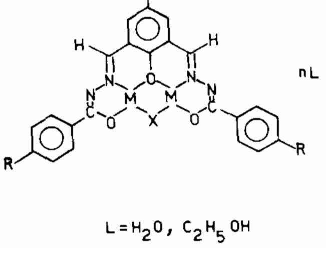
The ^1H n.m.r. (DMSO-d_6) of Ib shows: δ 12.73 (s, 1H, OH), δ 12.20 (s, 2H, NH); δ 8.70 (s, 2H, $=\overset{H}{C}\langle$); δ 7 76 (s, 2H, ); δ 7.61 (q, AA'BB', 8H ), δ 2.39 (s, 3H, $-CO-$$-CH_3$).

δ from $Si(CH_3)_4$ as internal standard

the literature [14], and the corresponding aroylhydrazine in absolute ethanol under reflux for 3 h. Generally by cooling the crystalline products precipitate as pale yellow needles. IR and ^1H NMR (dmso-d_6) are reported in Tables I and II.

The complexes of ligand Ia were synthesized by reaction with the corresponding metal chloride in ethanolic solution under reflux for 3 h in the presence of LiOH with the molar ratio 1.1:3; H_3L:MX_2:LiOH.

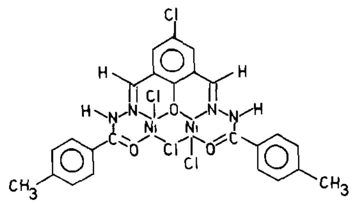
With the ligand Ib we used as a base 1,8-bis(dimethylamino)naphthalene (proton sponge). The homobinuclear complexes prepared are of the type

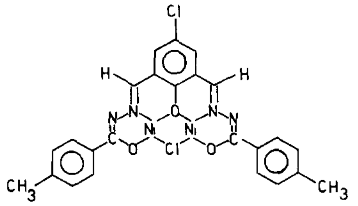


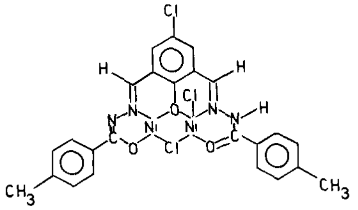
L = H_2O, C_2H_5OH

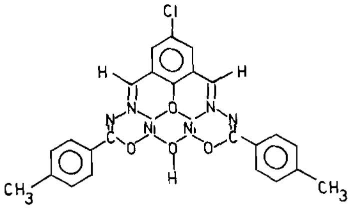
the organic moiety acting as pentadentate ligand capable of bridging together two similar metal ions through the phenolic oxygen. The nature of the second bridging group X strongly depends on the experimental conditions employed in the preparation of the complexes; in particular the reaction of ligand Ib with nickel(II) chloride in the presence of an excess of proton sponge gives rise to OH bridged binuclear complexes; on carrying out the reaction in the presence of different amounts of base, instead, mixtures containing chloride and variously deprotonated pentadentate ligands are obtained. A similar behaviour has been found also for vanadyl(IV), for which, with an excess of base, a bridging ethoxy group is present. With zinc(II), cobalt(II) and copper(II) dichloride, the chloride-bridged binuclear complexes have been found.

To verify the different behaviour of acidic protons in the ligand towards bases we have tried to prepare the whole series of binuclear nickel(II) complexes with the ligand Ib, which can act as neutral mono, di- or tribasic pentadentate ligand. By employing subsequent stoichiometric amount of a strong base (proton sponge, pK_a = 12.34) the following reaction scheme has been obtained:









The analytical and physico-chemical data agree with the formulation reported above.

The infrared spectra of this series show a decrease in the complexity of bands in the region 3500–3000 cm^{-1} on going from A to D. The complexes C and D show only a broad band at about 3425 cm^{-1}, due to the stretching frequencies of the water hydroxyl groups, while A and B also show bands due to N–H stretching at 3269, 3166 cm^{-1} (A) and 3189 cm^{-1} (B). A C=O stretching band at 1634 cm^{-1} for the complexes A (about 30 cm^{-1} lower than that in the free ligand which lies at 1660 cm^{-1}), present also in the complex B at 1637 cm^{-1} as a shoulder, completely disappears in thy complexes C and D. Moreover, in the complexes B, C and D bands are present centered at 1610 cm^{-1} due to the C=N–N=C stretching residue [12].

The analogous copper(II), nickel(II), cobalt(II), vanadyl(IV) and zinc(II) bis deprotonated complexes with the ligand Ia show an infrared spectrum comparable with those of C and D above reported. The electronic spectra of nickel(II) complexes in the solid state and in solution show d–d bands due to pseudo-octahedral geometry. ^1H NMR studies at variable temperature of the paramagnetic complexes and their thermogravimetric behaviour are in progress.

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