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SYNTHESIS AND CHARACTERIZATION OF COPPER AND NICKEL COMPLEXES WITH N-ARYLPYRROLE-2-ALDIMINES

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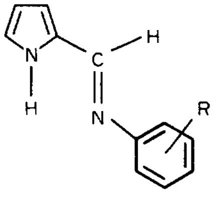
Abstract—A series of 17N-arylpyrrole-2-aldimine ligands has been synthesized by condensation of pyrrole-2-carboxaldehyde and substituted anilines. All CuL_2 complexes are square, whereas NiL_2 compounds are square, tetrahedral or eventually present a square $\rightleftharpoons$ tetrahedral equilibrium. Attempts of chemical oxidation have shown the existence of nickel(III) and copper(III) in solution.

Due to their good stability and their prominence in areas of biological interest, the metal chelate complexes of condensed pyrrole ring systems such as dipyrromethenes, phthalocyanines or porphyrins have been quite thoroughly studied and characterized. However, it is somewhat surprising that only a few complexes have been reported with ligands containing a single pyrrole ring. The coordination of pyrrole-2-aldimine with an alkyl group as a substituent of the imine function has been studied with colbalt(III),[1] nickel(II)[2] and copper(II).[2,3] On the other hand, N-arylpyrrole-2-aldimine metal complexes are unknown except for the copper(II) compounds with the N-*para*-substituted phenylpyrrole-2-aldimine,[4,5] and we report here on the coordination of nickel(II) and copper(II) with these ligands. A small difference in the electronic properties or steric requirements of Schiff bases can result in the formation of complexes with different geometrical configurations, which is why we have shown the influence of the nature and the *ortho*, *meta* or *para* position of the phenyl substituent on the structure of nickel(II) and copper(II) compounds. Moreover, the existence of a delocalized π system and the strong electron-donating power of the deprotonated pyrrole nitrogen atom could eventually allow the stabilization of unusual high oxidation states.



R = H, CH_3, OCH_3, OC_2H_5, Cl, Br or NO_2 in *ortho*, *meta* or *para* positions

H Pim – PhR

EXPERIMENTAL

All reagents and solvents used were of reagent-grade purity. Electronic spectra were recorded using a Perkin–Elmer Lambda 6 or a Beckman 5240 spectrophotometer and IR spectra with a Pye–Unicam SP3-300 spectrometer in KBr pellets or Nujol mulls. Proton NMR spectra were obtained on a Bruker AC 300 instrument in $CDCl_3$ or CD_3COCD_3 solution (300.13 MHz): chemical shifts were referred to internal Me_4Si. Magnetic susceptibilities were determined at room temperature (20°C) using $HgCo(SCN)_4$ as a calibrant; diamagnetic susceptibility corrections were calculated from Pascal's constants.[6] Conductance measurements were made with a CD 810 Tacussel apparatus calibrated with 10^{-3} mol dm^{-3} KCl.

Synthesis of the ligands

The ligands were prepared according to the method described in the literature,[4] which involved a condensation reaction of the pyrrole-2-aldehyde and the appropriate substituted aniline in a 1 : 1 molar ratio, using ethanol as a solvent (12 h stirring

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at room temperature). The oils were purified by flash chromatography (eluant 80% CH_2Cl_2, 20% $CH_3CO_2C_2H_5$) and the crude solids recrystallized in ethanol.

Synthesis of the copper(II) *complexes*

Copper(II) compounds were obtained using Tanaka and Yamauchi's method.[4] A mixture of copper(II) acetate and ligand in a 1 : 2 molar ratio was stirred for 12 h in ethanol at room temperature. After concentration, the solids precipitated.

Synthesis of the nickel(II) *complexes*

Based on the methol of Holm *et al.*,[1] the ligands (0.01 mol) and potassium t-butoxide (0.01 mol) were dissolved separately in anhydrous tetrahydrofuran and then mixed. Solid tetraethylammonium tetrabromonickelate(II) (0.005 mol) was then added. The mixture was stirred for 48 h at room temperature and filtered. The filtrate was reduced in volume to a dark oil which was crystallized *in vacuo*, after several hours in the case of *para*-substituted phenyl ligands (yield: 30%). For the other compounds, a few drops of ethanol were added to the oil; the complexes crystallized after 6 h stirring (yield: 10%).

All crude complexes were recrystallized from 70% n-hexane, 30% methylene chloride.

RESULTS AND DISCUSSION

Analytical and physical data for the ligands, copper(II) and nickel(II) complexes are given in Tables 1–3. The molar conductivity of the copper(II) and nickel(II) compounds in acetone is always lower than 2 S cm^2 mol^{-1}, in agreement with their neutral molecular structure.

The IR spectra indicate clearly the coordination of the two nitrogen donor atoms: the N—H stretching vibration in the ligands near 3240 cm^{-1} disappears upon copper(II) and nickel(II) complex formation and the C=N stretching frequency at 1625±5 cm^{-1} is shifted downwards 55 cm^{-1} after complexation.

Table 1. Analytical[a] and physical data for the ligands

Ligands	M.p. (°C)	Analysis C	 H	 N	ν(N—H)	ν(C=N)
H(Pim—Ph)	95	77.5	5.7	16.3	3240	1625
		(77.7)	(5.9)	(16.5)		
H(Pim—*p*-ClPh)	98	64.4	4.2	13.5	3240	1620
H(Pim—*m*-ClPh)	69	64.5	4.5	13.6	3200	1610
H(Pim—*o*-ClPh)	oil	64.7	4.3	13.4	3280	1620
		(64.6)	(4.4)	(13.7)		
H(Pim—*p*-BrPh)	108	53.2	3.4	11.3	3250	1620
H(Pim—*m*-BrPh)	71	53.1	3.6	11.1	3180	1600
H(Pim—*o*-BrPh)	oil	52.9	3.7	11.1	3280	1620
		(53.0)	(3.6)	(11.3)		
H(Pim—*p*-MePh)	103	78.3	6.6	15.0	3200	1625
H(Pim—*m*-MePh)	68	77.9	6.5	15.2	3200	1625
H(Pim—*o*-MePh)	80	78.0	6.8	15.0	3220	1620
		(78.3)	(6.5)	(15.2)		
H(Pim—*p*-MeOPh)	96	71.9	6.0	13.8	3250	1630
H(Pim—*m*-MeOPh)	oil	72.1	6.1	13.9	3300	1625
H(Pim—*o*-MeOPh)	107	71.8	6.2	13.8	3260	1620
		(72.0)	(6.0)	(14.0)		
H(Pim—*p*-EtOPh)	119	72.8	6.5	12.9	3230	1620
H(Pim—*m*-EtOPh)	52	72.7	6.7	13.0	3200	1620
H(Pim—*o*-EtOPh)	oil	73.1	6.4	12.9	3270	1615
		(72.9)	(6.5)	(13.1)		
H(Pim—*m*-NO_2Ph)	100	61.4	4.2	19.6	3250	1625
		(61.4)	(4.2)	(19.5)		

[a] Calculated values are given in parentheses. Analyses were performed in this University.

Table 2. Analytical[a] and physical data for copper(II) compounds

Compounds	Analysis			χ_M	μ_{eff}[b]	
	C	H	N	(10^6 c.g.s.u.)	(B.M.)	ν(C=N)
Cu(Pim—Ph)$_2$	65.6	4.4	13.8	1560	1.91	1570
	(65.8)	(4.5)	(14.0)			
Cu(Pim—*p*-ClPh)$_2$	56.3	3.6	11.7	2180	2.26	1570
Cu(Pim—*m*-ClPh)$_2$	56.2	3.3	12.0	1660	1.97	1550
Cu(Pim—*o*-ClPh)$_2$	56.0	3.4	12.0	1700	1.99	1550
	(56.1)	(3.4)	(11.9)			
Cu(Pim—*p*-BrPh)$_2$	47.4	2.9	10.0	2010	2.17	1570
Cu(Pim—*m*-BrPh)$_2$	47.1	2.9	9.8	1640	1.96	1550
Cu(Pim—*o*-BrPh)$_2$	47.5	2.9	9.9	2000	2.16	1550
	(47.2)	(2.9)	(10.0)			
Cu(Pim—*p*-MePh)$_2$	67.1	5.0	12.9	1620	1.95	1570
Cu(Pim—*m*-MePh)$_2$	66.9	5.0	13.2	1580	1.92	1570
Cu(Pim—*o*-MePh)$_2$	67.1	5.0	13.2	1620	1.95	1570
	(67.1)	(5.1)	(13.0)			
Cu(Pim—*p*-MeOPh)$_2$	62.3	4.6	12.0	1870	2.09	1570
Cu(Pim—*m*-MeOPh)$_2$	62.3	4.6	12.1	1920	2.12	1570
Cu(Pim—*o*-MeOPh)$_2$	62.3	4.6	12.1	1540	1.90	1560
	(62.4)	(4.8)	(12.1)			
Cu(Pim—*p*-EtOPh)$_2$	63.5	5.4	11.1	1640	1.96	1570
Cu(Pim—*m*-EtOPh)$_2$	63.9	5.2	11.4	1760	2.03	1565
Cu(Pim—*o*-EtOPh)$_2$	63.6	5.5	11.3	1610	1.94	1570
	(63.7)	(5.3)	(11.4)			
Cu(Pim—*m*-NO$_2$Ph)$_2$	53.9	3.1	17.2	1500	1.87	1570
	(53.7)	(3.3)	(17.1)			

[a] Calculated values are given in parentheses. Analyses were performed in this University or by the Microanalytical service of C.N.R.S.

[b] B.M. = 0.927×10^{-23} A m^2.

Table 3. Analytical[a] and physical data for nickel(II) compounds

Complexes	Analysis (%)			χ_M	
	C	H	N	(10^6 c.g.s.u.)	ν(C=N)
Ni(Pim—Ph)$_2$	66.8	4.7	14.0	Para[b] (2600)	1560
	(66.5)	(4.6)	(14.1)		
Ni(Pim—*p*-ClPh)$_2$	56.4	3.5	12.9	Para[b] (2150)	1570
Ni(Pim—*m*-ClPh)$_2$	57.0	3.5	12.0	Dia	1560
	(56.7)	(3.5)	(12.0)		
Ni(Pim—*p*-BrPh)$_2$	47.7	3.2	10.2	Dia	1570
Ni(Pim—*m*-BrPh)$_2$	47.9	3.0	10.1	Dia	1570
Ni(Pim—*o*-BrPh)$_2$	47.4	3.0	10.0	Dia	1560
	(47.6)	(2.9)	(10.1)		
Ni(Pim—*p*-MePh)$_2$	67.9	5.4	13.4	Dia	1570
Ni(Pim—*m*-MePh)$_2$	67.9	5.3	13.2	Dia	1570
Ni(Pim—*o*-MePh)$_2$	68.1	5.3	13.0	Dia	1560
	(67.8)	(5.2)	(13.2)		
Ni(Pim—*p*-MeOPh)$_2$	63.4	4.9	12.0	Dia	1560
Ni(Pim—*o*-MeOPh)$_2$	63.0	4.8	12.2	4150	1570
	(63.1)	(4.9)	(12.3)		
Ni(Pim—*p*-EtOPh)$_2$	64.6	5.6	11.6	Dia	1570
Ni(Pim—*m*-EtOPh)$_2$	64.6	5.6	11.4	Para[b] (1000)	1570
Ni(Pim—*o*-EtOPh)$_2$	64.4	5.5	11.6	4400	1560
	(64.4)	(5.4)	(11.5)		
Ni(Pim—*m*-NO$_2$Ph)$_2$	54.6	3.4	16.9	Para[b] (3700)	1560
	(54.3)	(3.3)	(17.3)		

[a] Calculated values are given in parentheses. Analyses were performed in this University or by the Microanalytical service of C.N.R.S.

[b] Magnetic susceptibilities of these compounds depend on the synthesis conditions.

Copper(II) *compounds*

The magnetic data always lie in the range expected for mononuclear d^9 copper(II) compounds. An example of their electronic spectra is given in Fig. 1 with a methyl substituent in the *para* position. All ligands on the one hand and copper(II) compounds on the other hand have similar spectra. The bands which can probably be assigned to $\pi \rightarrow \pi^*$ transitions[7] are very slightly shifted to higher wavelengths with *meta* and then *para* substituents. The band around 230 nm can be resolved into, at least, two components. The more energetic component (217 nm) does not seem influenced by the complexation. The second component and the other bands are shifted to the weak energies (3000–5000 cm^{-1}); these $\pi \rightarrow \pi^*$ transitions involving metal and ligand orbitals.[8] The large band (280–400 nm) is split into two bands in the copper(II) compounds around 310 and 370 nm. In the visible region, the absorbance is much weaker; all the copper(II) compounds exhibit a shoulder around 700 nm (ε = 180 $\text{dm}^3\ \text{mol}^{-1}\ \text{cm}^{-1}$). The similarity in electronic spectra seems to indicate the same square structure for all copper(II) compounds, as shown by Addison *et al.*[5] for the N-*para*-substituted phenylpyrrole-2-aldimine copper(II) complexes.

Nickel(II) *compounds*

Magnetic data and electronic spectra clearly show that these bis-chelate complexes can exhibit planar or tetrahedral structures. In the solide state, the diamagnetism of most of the compounds is in agreement with a square planar configuration and the paramagnetic susceptibility of N-*ortho*-alkoxy substituted complexes gives a tetrahedral configuration.

The paramagnetic susceptibility, much lower than 4000×10^{-6} for several complexes, is indicative of a mixture of the two configurations. However, solution electronic spectra show a planar structure for all the compounds except for the two tetrahedral complexes. We have tried to prepare the two forms in the solid state. Because the planar $\rightleftharpoons$ tetrahedral structural equilibrium is endothermic,[2] we have proved hot working complex syntheses to obtain the tetrahedral form: we have noted a higher magnetic susceptibility for the solid products in agreement with the increase in the tetrahedral form in the mixture, but the dissolution has always led to complete isomerization into the planar configuration.

The electronic spectra always show a band around 220 nm which is also observed in copper(II) complexes (Fig. 2). This band which does not seem influenced by the complexation can be assigned to a $\pi \rightarrow \pi^*$ intraligand transition. On the other hand, the $\pi \rightarrow \pi^*$ transitions probably involving metal and ligand orbitals depend on the geometrical configurations of the complexes: several $\pi \rightarrow \pi^*$ transitions appear in the 250–500 nm range in the square compounds whilst a large band (380–480 nm) is observed in the tetrahedral compounds. Two *d–d* transitions of tetrahedral nickel(II) can be observed: the first [ν_2: ${}^3T_1(F) \rightarrow {}^3A_2(F)$] at 1005 nm and the second [ν_3: ${}^3T_1(F) \rightarrow {}^3T_1(P)$] around 570 nm with a shoulder near 600 nm, assigned to a

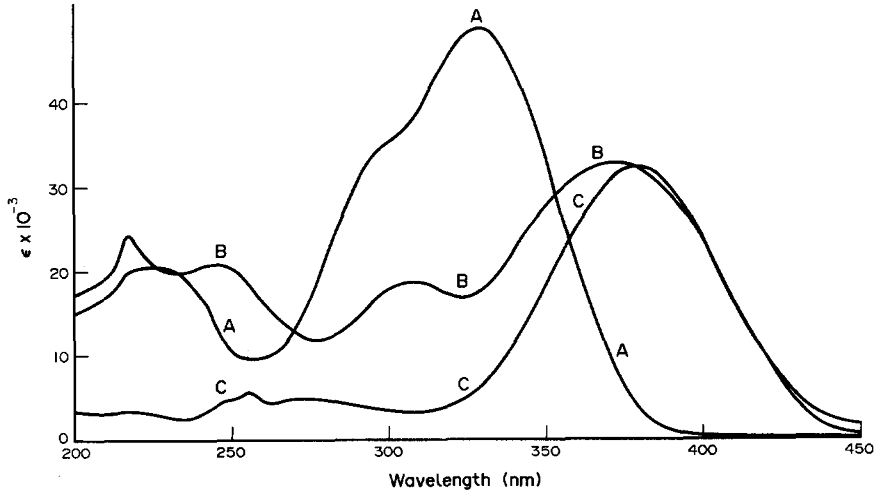

Fig. 1. Electronic spectra of ligand, copper(II) compound and protonated ligand: (A) HPim—p-CH_3Ph; (B) Cu(Pim—p-$CH_3Ph)_2$; and (C) [HPimH—p-$CH_3Ph)]^+ClO_4^-$.

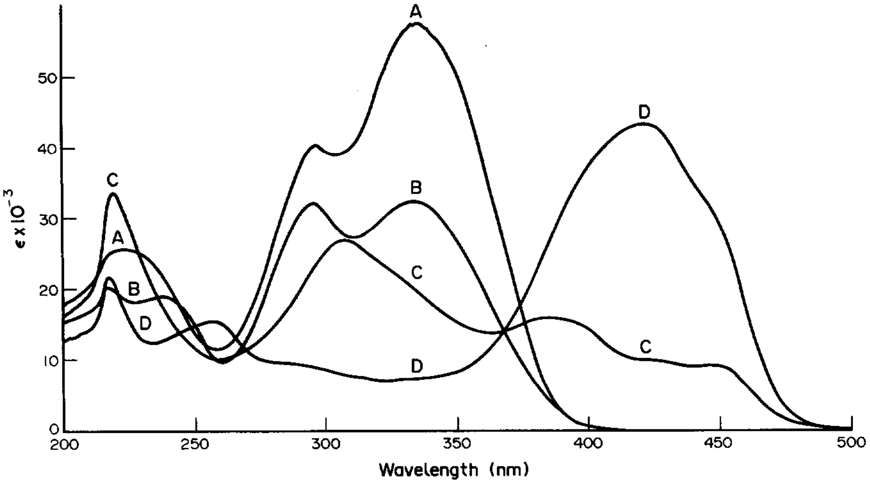

Fig. 2. Electronic spectra of ligands and nickel(II) compounds: (A) HPim—p-CH_3OPh; (B) HPim—o-CH_3OPh; (C) Ni(Pim—p-$CH_3OPh)_2$ (square); and (D) Ni(Pim—o-$CH_3OPh)_2$ (tetrahedral).

forbidden triplet–singlet transition. The ligand field parameters are obtained from transition energy ratios given by Lever.[9] The 10 Dq values (5000 cm^{-1} for the o-methoxy and 5300 cm^{-1} for the o-ethoxy substituted compounds) are in agreement with four nitrogen-atom tetrahedral surroundings. The high B values (910 and 895 cm^{-1}) are indicative of the great ionic character of the metal–ligand bond.

The proton resonance spectra show only one signal for the azomethine proton and the methyl or methoxy protons (if present), which means that the two ligands are equivalent, a *trans* configuration being favoured by the sterical strains.

Attempts at oxidation

The addition of $Fe(ClO_4)_3 \cdot 9H_2O$ in an 80% methylene chloride and 20% acetone mixture to the yellow–green solutions of Cu(Pim—PhR$)_2$ yields orange–brown solutions. In the case of Ni (Pim—PhR$)_2$ solutions, green–brown solutions are obtained after the addition of iron(III) ions. After 2 h the continuous variation method shows a stable break at 0.5, indicating a reaction in the 1 : 1 ratio, in agreement with the reaction $ML_2 + Fe^{3+} \rightarrow ML^+{}_2 + Fe^{2+}$, corrresponding to a mono-electronic transfer between the complex and the iron(III) ion which involves the stabilization of copper(III) and nickel(III) in solution.

The presence of an aryl group on the imino nitrogen donor atom is required to obtain copper(III) or nickel(III) complexes. Indeed, the trials to oxidize N-alkyl, N-benzyl or N-phenetylpyrrole-2-aldimine copper(II) or nickel(II) compounds have always led to a decomposition of the ligand.

The relative fragility of the imino group agrees with the fact that the ligands are electroactive and are destroyed at potentials near the redox potential of the M^{III}/M^{II} system and so an electrochemical determination of this value was not possible: all our studies with platinum or glassy carbon electrodes in different solvents (acetone, acetonitrile) have failed. Moreover, it also seems that the position and the electrodonor or electroattractor character of the substituents appear without great influence on the stabilization of M^{III} complexes in solution.

We have tried to synthesize solid-oxidized metal complexes: the copper(II) or nickel(II) compound (10^{-3} mol) and hydrated iron(III) perchlorate (10^{-3} mol) were stirred for 2 h at room temperature in a CH_2Cl_2–$(CH_3)_2CO$ mixture (80–20). After excess solvent evaporation n-hexane was added to induce the precipitation. The crude solids were dissolved in hot CH_2Cl_2 to eliminate insoluble iron salt. After concentration of the filtrate, orange crystals were obtained and dried *in vacuo*. **CAUTION**: The perchlorate compounds must be handled carefully due to their tendency to explode.

Analytical data, electronic, IR, ^1H NMR and mass spectra show that the orange compounds are the ionic protoned ligand $LH^+ClO_4^-$. The presence of the iminium group is confirmed by the fact that the molar conductivity[10] (around 100 S cm^2 mol^{-1} [10^{-3} mol dm^{-3} in acetone]) agrees with a 1 : 1 electrolyte. The fact that a small excess of perchloric acid does not react with the metal(II) complexes and that the presence of an oxidizing reagent is required for this reaction indicates that the protoned ligands were obtained after oxidation of the metal centre, thus releasing the ligands. The strong ionic character of the metal–ligand bond has been shown for nickel(II) compounds ($B = ca$ 900 cm^{-1}); this ionic character is greater in the oxidized compound, and therefore unfavourable for the stabilization of the higher oxidation state.

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