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LETTER

Cobalt complexes with *N*-arylpyrrole-2-aldimine: structural study by nuclear magnetic resonance

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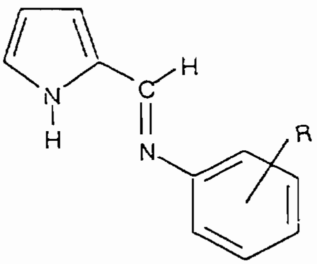
We have previously reported on the coordination of copper and nickel with *N*-arylpyrrole-2-aldimine: copper(II) compounds are virtually square planar whilst Ni(II) compounds are tetrahedral, planar or can exhibit a structural planar$\rightleftharpoons$tetrahedral equilibrium [1]. We wish to report here the characterization and the isomeric identification of cobalt complexes with *N*-arylpyrrole-2-aldimine.



HPim-RPh

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

Previously only some *N*-alkylpyrrole-2-aldimine [2] and tetradentate diimine pyrrole derivatives [3] of cobalt(III) have been studied.

Experimental

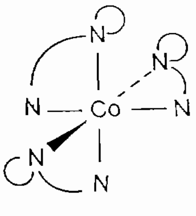
Physical measurements and the synthesis of the ligands have been described elsewhere [1]. The tris-(*N*-arylpyrrole-2-aldimine) cobalt(III) complexes were prepared according to the slightly modified Holm's procedure. Ligands (0.03 mol), potassium-t-butoxide (0.03 mol) and $[(C_2H_5)_4N]_2[CoBr_4]$ (0.01 mol) were mixed in dry THF. After 24 h of stirring at room temperature, the reaction mixture was filtered and the filtrate was evaporated to an orange oil. A few drops of ethanol induced precipitation of the solids. All crude complexes were recrystallized from n-hexane/methylene chloride (70/30).

Results and discussion

Analytical, diamagnetism, molar conductivity ($\Lambda <$ 2 S cm^2 mol^{-1} in 10^{-3} acetone) [4] and IR spectra (disappearing of the N–H stretching vibration and the down shift around 50 cm^{-1} of the C=N stretching frequency) are consistent with neutral octahedral molecular cobalt(III) complexes (Table 1). This means that cobalt(II) has been smoothly oxidized to cobalt(III) by air without any other oxidizing agent present.

Tris-chelate metal complexes containing three identical unsymmetrical bidentate ligands can exist in *fac* and *mer* configurations. The *fac* isomer shows a three-fold rotation axis whereas the *mer* isomer has no symmetry: the ligands are equivalent in the *fac* isomer and non-equivalent in the *mer* isomer. Therefore ^{1}H NMR spectra must present a single resonance for *fac* and three for *mer* compounds as shown by Fay and Piper [5] for unsymmetrical β-diketone complexes. Each proton resonance appears in the form of three signals. Aryl and pyrrolic proton resonances overlap in the 5–7 ppm region, but the H–C=N– and alkyl or alkoxy substituents protons when they are present, show three signals of equal intensity. These results are given in Table 2.

The chemical shifts are identical with the same substituent in the *para*, *meta* or *ortho* position. All these spectra are in good agreement with a *mer* configuration for all studied compounds.



mer

One of our goals is the stabilization of higher oxidation states of transition metals: solutions of orange cobalt(III) complexes (80% methylene chloride, 20% acetone) are

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TABLE 1. Analytical[a] and physical data for *N*-arylpyrrole-2-aldimine cobalt(III) complexes

Complexes	Melting point (°C)	C	H	N	νC=N
Co(Pim-Ph)$_3$	218	70.2	4.7	14.5	1570
		(70.0)	(4.8)	(14.8)	
Co(Pim-*p*BrPh)$_3$	223	49.4	2.8	10.3	1560
Co(Pim-*m*BrPh)$_3$	214	49.7	3.0	10.4	1555
Co(Pim-*o*BrPh)$_3$	210	49.3	2.9	10.6	1560
		(49.3)	(3.0)	(10.5)	
Co(Pim-*p*ClPh)$_3$	234	59.4	3.6	12.5	1565
Co(Pim-*m*ClPh)$_3$	198	59.1	3.8	12.7	1560
Co(Pim-*o*ClPh)$_3$	222	59.1	3.8	12.5	1560
		(59.2)	(3.6)	(12.6)	
Co(Pim-*p*CH$_3$Ph)$_3$	217	70.8	5.7	13.8	1565
Co(Pim-*m*CH$_3$Ph)$_3$	206	71.3	5.4	13.9	1560
Co(Pim-*o*CH$_3$Ph)$_3$	278	71.3	5.4	13.6	1560
		(71.1)	(5.4)	(13.8)	
Co(Pim-*p*CH$_3$OPh)$_3$	214	65.7	5.0	12.7	1560
Co(Pim-*m*CH$_3$OPh)$_3$	151	65.6	5.2	12.9	1565
Co(Pim-*o*CH$_3$OPh)$_3$	232	65.8	5.3	12.5	1560
		(65.9)	(5.0)	(12.8)	
Co(Pim-*p*C$_2$H$_5$OPh)$_3$	204	66.7	5.6	12.0	1565
Co(Pim-*m*C$_2$H$_5$OPh)$_3$	242	67.4	5.5	12.0	1560
Co(Pim-*o*C$_2$H$_5$OPh)$_3$	213	66.9	5.6	11.8	1565
		(67.1)	(5.6)	(12.0)	
Co(Pim-*m*NO$_2$Ph)$_3$	188	56.3	3.4	18.1	1565
		(56.5)	(3.4)	(18.0)	

[a]Calculated values are given in parentheses. Analyses were performed by the microanalytical service of CNRS.

TABLE 2. Chemical shift for some *N*-arylpyrrole-2-aldimine cobalt(III) complexes

R	δH–C=N	δCH$_3$–	δCH$_2$–
CH$_3$–	7.30	2.20	
	7.35	2.30	
	7.40	2.35	
CH$_3$–O–	7.30	3.65	
	7.40	3.70	
	7.45	3.75	
CH$_3$–CH$_2$–O–	7.30	1.00 t	3.60 q
	7.35	1.20 t	3.75 q
	7.45	1.30 t	3.90 q

t: triplet; q: quadruplet.

oxidized into brown cobalt(IV) solutions by ion(III) perchlorate. The continuous variations method with a stable break at 0.5 ratio indicates a reaction in the 1:1 ratio: $Fe^3+CoL_3 \rightleftharpoons Fe^2+CoL_3$. A crude brown solid was obtained after concentration of equimolar Co(III) complex and iron(III) solution. The analyses are not very satisfactory, nevertheless magnetic susceptibility (one unpaired electron), IR and electronic spectra indicate a low spin cobalt(IV) compound. Unfortunately, all attempts to recrystallize these solids are unsuccessful, the cobalt(IV) complexes being in part again reduced to cobalt(III).

References

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