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Preparation, Proton Resonance and Infrared Studies of Chromium(III) Complexes of some Aldimines

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Information on Schiff base complexes with monodentate ligands of type $XC_6H_4CH{=}NC_6H_4Y$, X = Cl, OMe, Me; Y = NO_2, Me, Cl, does not seem to have appeared in the literature. Interest seems to have been centred on Schiff bases having two or more coordinating sites [1–8]. In some of these polydentate ligands, not all the available binding sites are utilized.

In this work we report and discuss: (i) the preparation of some Schiff base complexes of chromium(III); (ii) the proton resonance and infrared spectroscopic properties of these complexes.

Experimental

Physical Methods

The infrared spectra were recorded on a Perkin-Elmer 257 grating spectrometer. The proton NMR spectra were recorded on a Varian HA100D with $CDCl_3$ as solvent, and the elemental analysis was carried out on a Perkin-Elmer 240 microanalyser.

Preparation of the Schiff Base Ligands

The aldimine–Schiff base ligands were prepared by reacting the corresponding benzaldehyde or substituted benzaldehyde with the corresponding aniline or substituted aniline in equimolar proportions using ethanol as solvent as indicated in a previous paper [9].

Complex Formation

Chromium(III) chloride purchased from BDH chemicals was found suitable for this preparation and did not need further purification. It was reacted with the Schiff base ligand in a molar ratio of 1:3 using ethanol as solvent. In most cases crystallization was not immediate and so it was induced by concentrating the solution. The prepared complexes together with the analytical data are shown in Table I.

Results and Discussion

Infrared Evidence

The infrared spectral data (Tables II–IV) of the ligands and the complexes in the 4000–600 cm^{-1} range have been interpreted on the basis of previously

TABLE I. Elemental Analysis[a] of the Chromium(III) Complexes of some Aldimines

	C	H	N	Colour
$(C_6H_5CH{=}NC_6H_4NO_2)\cdot CrCl_3$	56.10 (56.25)	3.63 (3.60)	10.06 (10.10)	brown
$(ClC_6H_4CH{=}NC_6H_4NO_2)_3\cdot CrCl_3$	49.80 (49.78)	2.91 (2.87)	8.97 (8.94)	yellow green
$(OMeC_6H_4CH{=}NC_6H_4Me)_3\cdot CrCl_3$	64.63 (64.67)	5.19 (5.39)	5.06 (5.02)	black
$(OMeC_6H_4CH{=}NC_6H_4Cl)_3\cdot CrCl_3$	56.05 (56.12)	3.95 (4.00)	4.70 (4.67)	greenish black
$(MeC_6H_4CH{=}NC_6H_4Cl)_3\cdot CrCl_3$	60.00 (59.78)	4.30 (4.27)	5.05 (4.98)	green
$(C_6H_5CH{=}NC_6H_5)_3\cdot CrCl_3$	66.50 (66.47)	4.71 (4.68)	6.00 (5.96)	green
$(ClC_6H_4CH{=}NC_6H_5)_3\cdot CrCl_3$	57.85 (57.80)	3.67 (3.70)	10.91 (10.88)	yellow green
$(OMeC_6H_4CH{=}NC_6H_5)_3\cdot CrCl_3$	63.15 (63.23)	4.55 (4.52)	5.30 (5.26)	black
$(MeC_6H_4CH{=}NC_6H_5)_3\cdot CrCl_3$	67.80 (67.83)	4.77 (4.80)	5.69 (5.65)	black

[a] Calculated values are given in parentheses.

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TABLE II. Important Infrared Spectral Data (cm^{-1}) of the Chormium(III) Complexes with some Aldimines

Complex	C=N	Cr–N	C–H (alkane)
$(C_6H_5CH=NC_6H_4NO_2)_3\cdot CrCl_3$	1640–1660	610–620	
$(ClC_6H_4CH=NC_6H_4NO_2)_3\cdot CrCl_3$	1630–1645	610–620	
$(OMeC_6H_4CH=NC_6H_4Me)_3\cdot CrCl_3$	1640–1710	610–620	3040
$(OMeC_6H_4CH=NC_6H_4Cl)_3\cdot CrCl_3$	1630–1710	610–620	3025
$(MeC_6H_4CH=NC_6H_4Cl)_3\cdot CrCl_3$	1630–1650	610	2020
$(C_6H_5CH=NC_6H_5)_3\cdot CrCl_3$	1650	610	
$(ClC_6H_4CH=NC_6H_5)_3\cdot CrCl_3$	1640	610	
$(OMeC_6H_4CH=NC_6H_5)_3\cdot CrCl_3$	1630–1640	610–620	3025
$(MeC_6H_4CH=NC_6H_5)_3\cdot CrCl_3$	1640	610	3020

TABLE III. Ring Vibrational Modes (cm^{-1})

Compound	Stretching	Bending
$(C_6H_5CH=NC_6H_4NO_2)_3\cdot CrCl_3$	1630, 1520, 1450, 1340, 1230	1110, 1050, 845
$(ClC_6H_4CH=NC_6H_4NO_2)_3\cdot CrCl_3$	1620, 1510, 1430, 1350, 1220	1160, 1040, 920
$(OMeC_6H_4CH=NC_6H_4Me)_3\cdot CrCl_3$	1630, 1525, 1440, 1330, 1230	1140, 1030, 860
$(OMeC_6H_4CH=NC_6H_4Cl)_3\cdot CrCl_3$	1620, 1540, 1420, 1320, 1220	1110, 1020, 840
$(MeC_6H_4CH=NC_6H_4Cl)_3\cdot CrCl_3$	1630, 1530, 1425, 1330, 1230	1140, 1030, 850
$(C_6H_5CH=NC_6H_5)_3\cdot CrCl_3$	1610, 1520, 1430, 1430, 1210	1115, 1030, 850
$(ClC_6H_4CH=NC_6H_5)_3\cdot CrCl_3$	1630, 1530, 1420, 1320, 1220	1120, 1040, 830
$(OMeC_6H_4CH=NC_6H_5)_3\cdot CrCl_3$	1615, 1520, 1430, 1320, 1210	1110, 1030, 840
$(MeC_6H_4CH=NC_6H_5)_3\cdot CrCl_3$	1620, 1530, 1430, 1315, 1220	1115, 1030, 850

TABLE IV. Absorptions due to Substituents (cm^{-1})

Compound	CH_3(sym) bending mode	(C–C)	CH rocking	C–H stretch
$(C_6H_5CH=NC_6H_4NO_2)_3\cdot CrCl_3$				
$(ClC_6H_4CH=NC_6H_4NO_2)_3\cdot CrCl_3$				
$(OMeC_6H_4CH=NC_6H_4Me)_3\cdot CrCl_3$	1390s	940m	1020s	1040m
$(OMeC_6H_4CH=NC_6H_4Cl)_3\cdot CrCl_3$	1400m	920s	1020s	1050m
$(MeC_6H_4CH=NC_6H_4Cl)_3\cdot CrCl_3$	1385	910s	1010m	1030m
$(C_6H_5CH=NC_6H_5)_3\cdot CrCl_3$				
$(ClC_6H_4CH=NC_6H_5)_3\cdot CrCl_3$				
$(OMeC_6H_4CH=NC_6H_5)_3\cdot CrCl_3$	1405m	930s	1030s	1040m
$(MeC_6H_4CH=NC_6H_5)_3\cdot CrCl_3$	1395w	920s	1020m	1040m

reported data [10–14]. The eight vibrational modes of the phenyl group (Table III), five stretching and three bending, lie in the 1630–1220 and 1160–840 cm^{-1} regions respectively. The bands in the 1495–1944 cm^{-1} range are due to the CH_3 symmetrical bending mode, while those near the 910–930 cm^{-1} range are the ν(C–C) stretching vibrations. Absorptions in the 1010–1030 cm^{-1} region are due to the C–H stretching vibrations [15–17]. It has been observed that sharp bands in the 1620–1635 cm^{-1} region of Schiff base complexes are assigned to ν(C=N) [18]. However, in most of these complexes, this band appears in the 1645–1660 cm^{-1} region. The observed shift to higher frequencies in these complexes suggests a coordination through the azomethine nitrogen to the metal moiety [19, 20]. In the aldimine chromium(III) complexes a similar frequency shift is observed, for example the ν(C=N) occurs at the 1630–1650 cm^{-1} region and implies a coordination through the azomethine nitrogen to the chromium(III) ion. The Cr(III)–N bonding in these complexes is also observed in the 610–620 cm^{-1} region which is in agreement with observations of Biradar and co-workers [12, 13].

Proton NMR Evidence

The spectrum of 4-chlorophenyl, 3-methylbenzaldimine for example is characterized by three signals

TABLE V. The ^1H NMR Spectral Data[a] of the Prepared Chromium(III) Complexes with some Aldimines

Complex	Methine protons	Phenyl protons	Methyl and ethyl protons
$(C_6H_5CH{=}NC_6H_4NO_2)_3\cdot CrCl_3$	8.4	6.9–7.5	
$(ClC_6H_4CH{=}NC_6H_4NO_2)_3\cdot CrCl_3$	8.4	6.9–7.5	
$(OMeC_6H_4CH{=}NC_6H_4Me)_3\cdot CrCl_3$	8.35	6.9–7.5	3.5, 1.6–1.4
$(OMeC_6H_4CH{=}NC_6H_4Cl)_3\cdot CrCl_3$	8.3	7.3–7.5	3.5
$(MeC_6H_4CH{=}NC_6H_4Cl)_3\cdot CrCl_3$	8.3	7.0–7.5	1.5
$(C_6H_5CH{=}NC_6H_5)_3\cdot CrCl_3$	8.3	7.0–7.5	
$(ClC_6H_4CH{=}NC_6H_5)_3\cdot CrCl_3$	8.3	7.0–7.5	
$(OMeC_6H_4CH{=}NC_6H_5)_3\cdot CrCl_3$	8.3	7.0–7.5	3.5
$(MeC_6H_4CH{=}NC_6H_5)_3\cdot CrCl_3$	8.4	7.0–7.5	1.5

[a] Chemical shifts in ppm relative to TMS.

at $\delta = 9.05$, 6.8–7.80 and 2.50 ppm (relative to TMS), attributed to the methine proton of the azomethine moiety, the phenyl protons and the methyl protons. Resonance shifts to higher frequencies are observed (Table V) for the complexes at the corresponding positions giving $\delta = 8.3$–8.40, 6.9–7.50 and 1.40–1.80 ppm for the azomethine proton, phenyl proton and methyl proton respectively. The observed shift to higher frequencies is indicative of coordination of the ligand to the chromium(III) ion through the nitrogen atom.

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