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THE PREPARATION, PROPERTIES OF HIGH- SPIN CHROMIUM(II) COMPLEXES AND X-RAY POWDER DIFFRACTION STUDY OF 3-CHLOROANILINIUM CHROMIUM CHLORIDE AND 3-CHLOROANILINIUM COPPER CHLORIDE COMPLEXES.

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Abstract

The compounds of chromium(II) have been prepared under anerobic conditions and investigated by Spectroscopic, magnetic susceptibility and, in a few instances, x-ray poweder techniques. New halogenochromate(II) complexes $[3\text{-}ClC_6H_4NH_3]_8[CrCl_6]Cl_4$, $[4\text{-}HOC_6H_4NH_3]_4[CrCl_6]$ and $[1\text{-}MepipzH_2]_3[CrCl_6]Cl_2$ have been Characterized.

The salts are magnetically-normal, high-spin, chromium(II)-compounds, Reflectance spectra are as expected for highly distorted complexes, confirming the six-coordinate octahedral structure.

X-ray powder diffraction study of 3-chloroanilinium chromium chloride and 3-chloroanilinium copper chloride complex which show that the complexes have different structures.

Introduction

Magnetically-dilute chromium(II) compounds show paramagnetism with effective magnetic moments close to spin-only value of 4.90 B.M. which do not vary with temperature. Simple paramagnetism arises because the individual para magnetic centres are independent of their neighbours and there is no magnetic exchange between the metal atoms. These types of complexes obey the Curie Law ($\chi_A = C/T$).

Complexes of high-spin chromium(II) ($t^3_{2g}\ eg^1$ configuration) and copper (II) $t^6_{2g}\ eg^3$ configuration) are often structurally similar because both lead to Jahn-Teller distortion. Consequently, cations known to stabilise known $[CuX_4]$ complexes have been used in the preparation of new chromium(II) complexes. It is possible that Chromium(II) complexes will show the same types of structures as the copper(II) complexes.

The dihydrates of the type $A_2[CrX_4(H_2O)_2]$ (A = NH_4, Rb, Cs, $PhNH_3$ 0.5 $pipzH_2$, PyH, X = Cl[1-2] A = NH_4, Rb, Cs, PyH, X = Br[3] have been isolated from solutions of constituents in suitable solvents. The complexes are magnatically dilute and high-spin[3,1,2] with reflectance spectra as expected for tetragonally-distorted octahedral anions $[CrX_4(H_2O)_2]^{2-}$ except for $[PyH]_2[CrBr_4(H_2O)_2]$ which

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contains[4] discrete trans-planar $CrBr_2(H_2O)_2$ units instead of the expected distorted octahedral anions $[CrBr_4(H_2O)]^{2-}$.

2-Experimental

2.1 Octakis(3-chloroanilinium) hexachlorochromate(II) tetrachloride.

Chromium(II) chloride tetrahydrate (2.2 g, 0.01 mole) was dissolved in a mixture of concentrated HCl (70 cm^3) and water (30 cm^3). To the resulting clear blue solution 3-chloroaniline (ca.4 cm^3, 0.03mole) was added. The white precipitates obtained dissolved on heating and the clear blue solution was allowed to cool slowly overnight. The white crystals which appeared were filtered off, washed with diethylether (50 cm^3) and dried under vacuum for five hours.The white compound turned green in two hours in air (yield 70%), Anal, Found C, 39.28: H, 4.05; N, 7.57; Cl, 24.72; Cr, 4.35 Calc. for $C_{48}H_{56}N_8Cl_{18}Cr$; C, 40.17; H, 3.93; N, 7.80; Cl, 24.73; Cr, 4.38%.

Table 3.1

Magnetic Susceptibility Data

Halogeno Complexes of Chromium(II)

Compound	T (K)	χ_A x10^6	$1/\chi_A$ x10^{-1}	μ_{eff} (B.M)
$3\text{-}ClC_6H_4NH_3]_8$-	293	9632	10.40	4.75
$[CrCl_6]Cl_4$	265	10812	9.25	4.78
	230	12348	8.09	4.76
	200	14425	6.93	4.80
	165	17338	5.76	4.78
	136	21554	4.64	4.84
$\theta = 4^0$	105	28166	3.55	4.86
	90	33131	3.02	4.88
Diamagnetic correction = -747 c.g.s units per mole				
$[4\text{-}HOC_6H_4NH_3]_4$.	293	9839	10.16	4.80
$[CrCl_6]$	265	11060	9.04	4.84
	230	12663	7.89	4.82
	200	14657	6.82	4.84
	165	17547	5.77	4.77

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	136	21621	4.62	4.84
	105	28184	3.54	4.86
$\theta = 0^{o}$	90	32544	3.07	4.83

Diamagnetic correction = 309 c.g.s units per mole

$[1\text{-Me-pipzH}_2]_3$	293	11919	8.39	5.28
$[CrCl_6]Cl_2$	265	13545	7.38	5.39
	230	15224	6.56	5.29
	200	17676	5.65	5.31
	165	20847	4.79	5.24
	136	25591	3.90	5.27
	105	33666	2.97	5.31
$\theta = O^{o}$	90	38703	2.58	5.27

Diamagnetic correction = -407c.g.s. units per mole

2.2- Tetrakis(4-hydroxyanilinium) hexachlorochromate(II)

Chromium(II) chloride tetrahydrate (2.52 g, 0.0129 mole) was dissolved in absolute ethanol (50 cm^3). To this was added 4-hydroxyanilinium chloride (3.76 g, 0.025 mole) dissolved in absolute ethanol (40 cm^3). Immediately a white solid appeared which was re-dissolved by heating to reflux with constant stirring. The solution was left to cool overnight, No compound appeared so the reaction mixture was concentrated to half volume and a light green compound which appeared from the green solution was filtered off, washed with absolute ethanol (30 cm^3) and dried under vacuum at room temperature for six hours. Its colour turned to dark green in five minutes in air (Yield 70%). Anal. Found C, 40.46; H, 4.77; N, 7.71; Cl, 30.02, Cr, 7, 50; Calc. for $C_{24}H_{32}N_4O_4Cl_6Cr$, C, 40.85; H, 4.57; N, 7.94; Cl, 30.18; Cr, 7.37%.

2-3 Tris(1-methylpiprazinium) hexachlorochromate(II). dichloride.

Chromium(II) chloride tetrahydrate (2.08 g, 0.01 mole) was dissolved in methanol (50 cm^3). To this was added 1-methylpiprazinium chloride (3.69 g, 0.02 mole). A blue solid separated immediately from the sky blue solution which was heated with continuous stirring to dissolve the solid. The reaction mixture was then allowed to cool overnight in an oilbath. No compound appeared so the reachtion mixture was concentrated to half volume when a light green compound separated which was filtered off, washed with methanol (30 cm^3) and diethylether (20 cm^3) and dried under vacuum at room temperature for five

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hours. The compound turned dark green in two minutes in air (yield 65%) Anal. Found C, 29.03; H, 6.82, N, 12.87; Cl, 44.02; Cr, 8.21; Calc. for $C_{15}H_{42}N_6Cl_8Cr$, C, 28.03; H, 6.58; N, 13.07; Cl, 44.20; Cr, 8.09%.

3- Results and Discussion

3.1. Magnetic Properties

The variation with temperature of the atomic susceptibility and effective magnetic moments of the complexes over the range 90-293K, and the Curie-Weiss constants, θ, are shown in table 3.1 and typical examples are plotted in figure/3.1

3-2 Normal Paramagnetic Complexes

The magnetic moments of the complexes $[3\text{-}ClC_6H_4NH_3]_8[CrCl_6]Cl_4$, $[4\text{-}HOC_6H_4NH_3]_4[CrCl_6]$ and $[1\text{-}MepipzH_2]_3[CrCl_6]Cl_2$ are close to the spin-only value (4.90 B.M.) and show little variation with temperature. The compounds are thought to be magnetically-normal, six-coordinate high-spin chromium(II) complexes and not to have polymeric bridged structures[2,5].

3-3 Reflectance Spectra

The reflectance spectra of the mentioned chromium(II) complexes are illustrated in Figures 3.2 seem to contain unbridged six-coordinate chromium(II) units, since they are magnetically normal. The reflectance spectra contain one broad absorption band in the region of 11000-12000 cm^{-1} as found for higly distorted complexes. This confirms the six-coordinate octahedral structure for these compounds.

3-4 X-Ray Powder Diffraction Study of

3-Chloroanilinium Chromium chloride and

3- Chloroanilinium Copper chloride complexes.

The copper(II) complexes $[3\text{-}ClC_6H_4NH_3]_8[CuCl_6]Cl_4$ has been shown[6] by X-ray crystal structure investigations to consists of discrete 3-Chloroanilinium cations, discrete $[CuCl_6]^{4-}$ anions and uncoordinated chloride ions. The cations have no unique structural features. Magnetic susceptibility data show evidence of weak antiferromagnetic interation between the hexachlorocuprate anions. The $[CuCl_6]^{4-}$ ion in $[3\text{-chloranilinium}]_8[CuCl_6]Cl_4$ has compressed tetragonal geometry.

Single crystal of the chromium(II) complex $[3\text{-}ClC_6H_4NH_3]_8[CrCl_6]Cl_4$ were isolated but were not suitable for X-ray investigation. Consequently, X-ray Powder diffraction photographs of both compounds were taken for comparison. The data are shown in table 3.4.2.

The copper(II) complex was prepared by the described method. The results show that the complexes have different structures, but do not exclude the presence of $[CrCl_6]^{4-}$ ions in the chromium(II) complex.

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Table 3.4

$[3\text{-}ClC_6H_4NH_3]_8[CrCl_6]Cl_4$			$[3\text{-}ClC_6H_4NH_3]_8[CuCl_6]Cl_4$		
White			Greenish yellow		
klhθ (degree)	hkld (Å)	I	θhklθ (degree)	hkld (Å)	I
12.70	3.47	s	12.88	3.45	s
12.45	3.57	s	17.27	2.59	s
			12.96	3.34	s
			9.83	4.50	s
			9.11	4.86	s
			17.18	2.60	s
10.33	4.29	m	11.78	3.77	m
14.40	2.77	m	11.23	3.95	m
11.2	3.96	w	10.52	4.21	m
13.32	3.09	w	8.86	4.99	m
16.12	2.77	w	13.42	3.31	m
16.73	2.67	w	13.8	3.22	m
17.43	2.57	w	15.01	2.97	m
4.52	9.76	w	18.3	2.45	w
5.65	7.82	w	23.98	1.89	w
11.20	3.96	w	26.28	1.73	w
18.57	2.41	w	19.67	2.28	vw
27.12	1.68	vw	27.50	1.66	vw

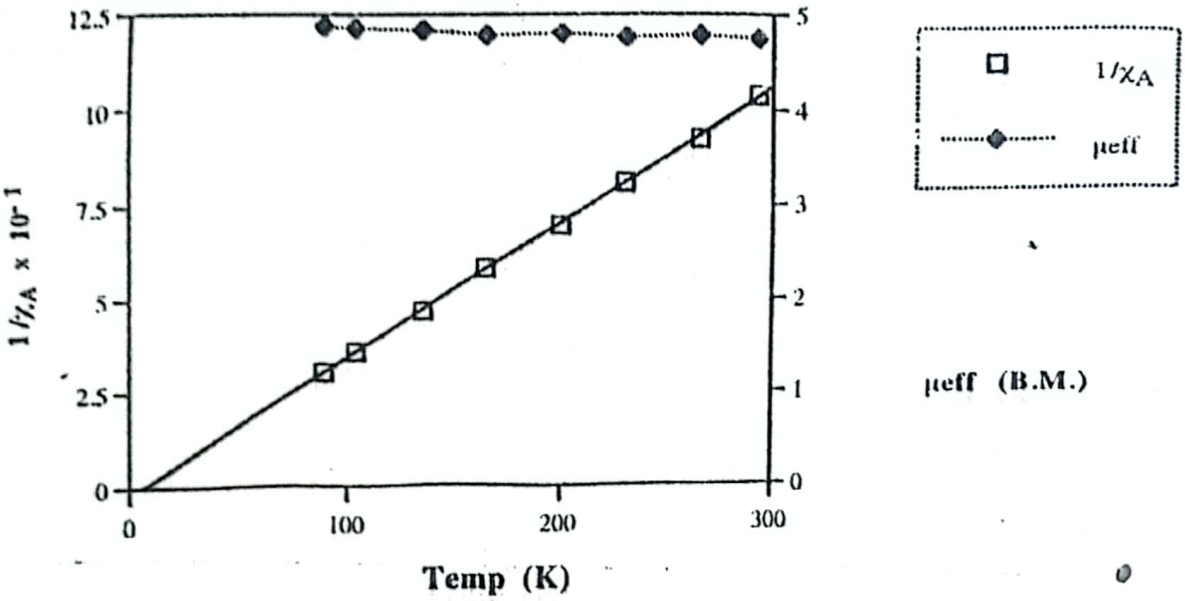
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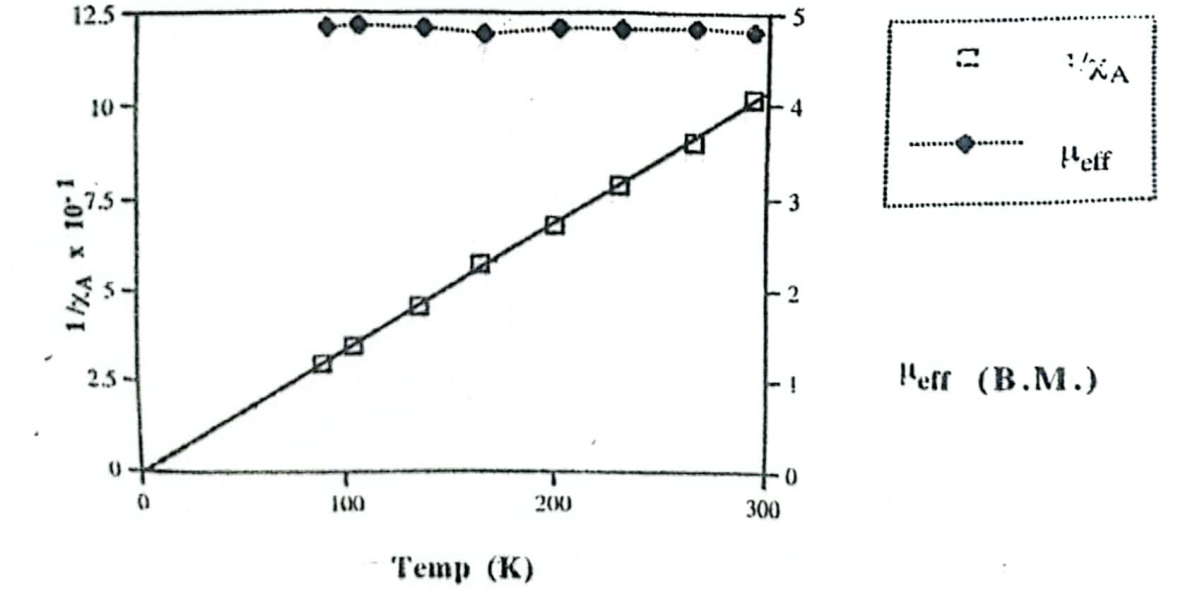
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Figure 3.6

$[3\text{-}ClC_6H_4NH_3]_8[CrCl_6]Cl_4$



$[4\text{-}HOC_6H_4NH_3]_4[CrCl_6]$



$[1\text{-Me-pipzH}_2]_3[CrCl_6]Cl_2$

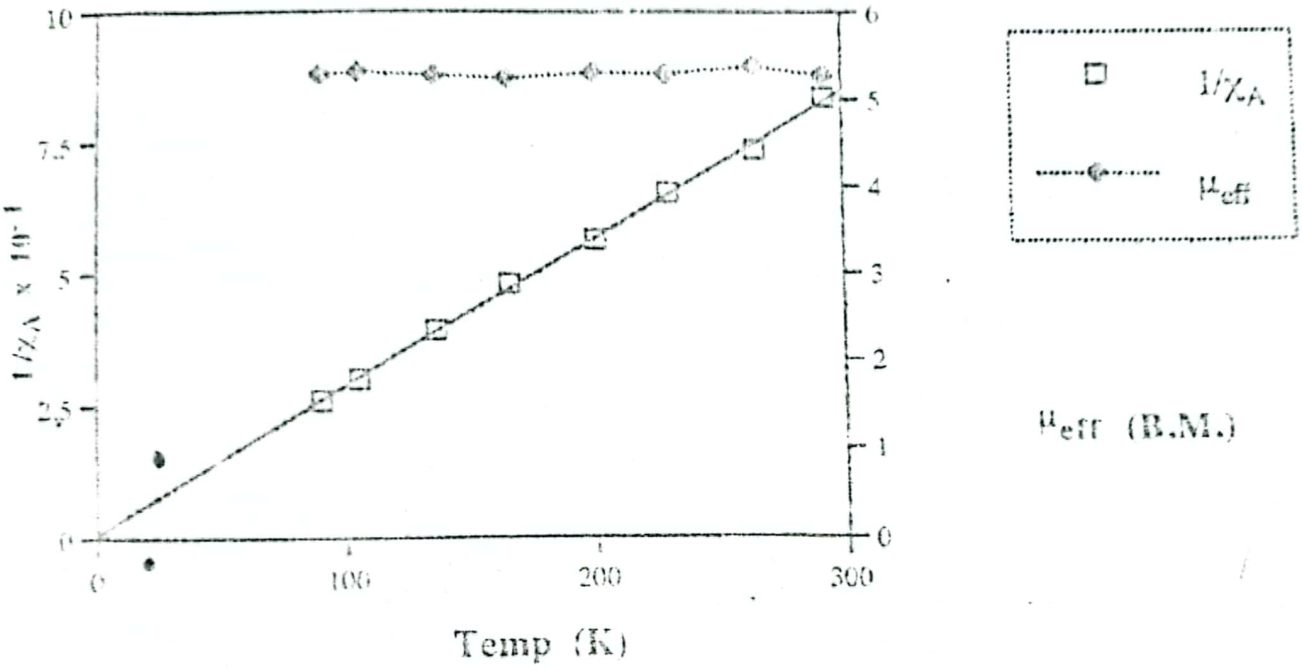
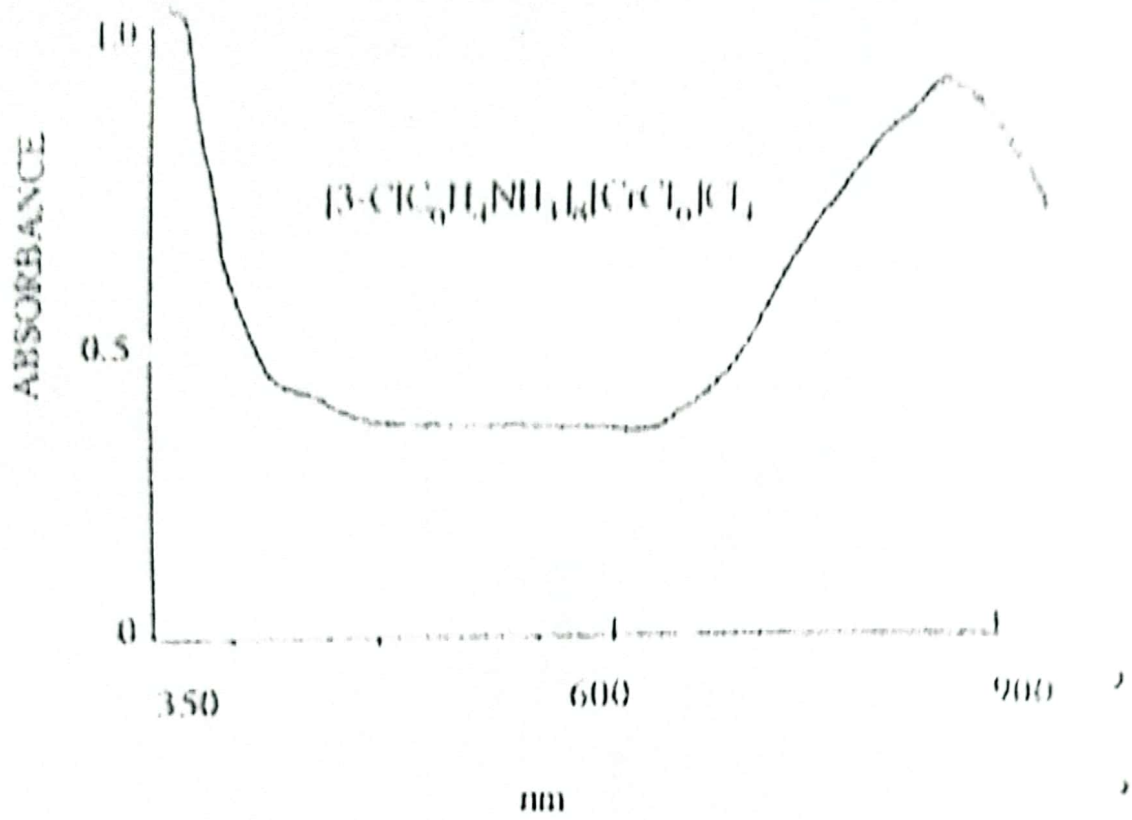
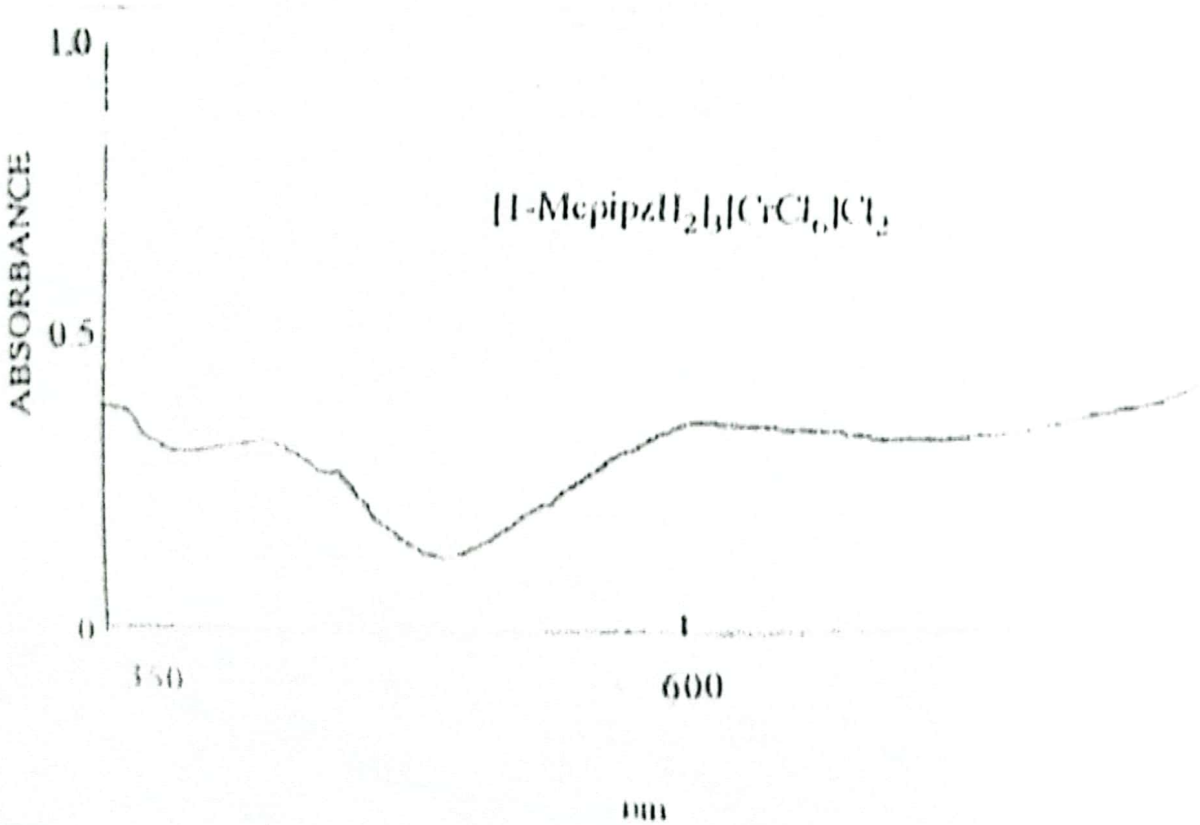


Figure 3.24


1.0
0.5
0
ABSORBANCE
[3-ClC6H4NH3]4[CrCl6]Cl4
350
600
900
nm


1.0
0.5
0
ABSORBANCE
[1-MepipzH2]3[CrCl6]Cl2
350
600
nm