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Synthesis and Characterization of Chromium(III) and Manganese(III) Complexes with a Hydrazone Derived from Pyrazolone and β-Diketone

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Novel complexes of chromium(III) and manganese(III) have been synthesized with a multidentate ligand 1,2-dihydro-1-phenyl-2,3-dimethyl-4-[2′,4′-pentanedione-3′-hydrazono]pyrazol-5-one. The complexes were characterized using elemental analysis, conductance measurements, magnetic susceptibility, thermal, infrared and electronic spectral studies. The ligand is neutral bidentate in all the chromium(III) complexes with the composition $[CrL_2X_2]X$ where X = Cl, Br, NO_3, ClO_4 and is neutral tridentate in the manganese(III) complexes with compositions $[MnL_2]X_3$ where X = Cl, Br and $[MnLX_3]$ where X = NO_3, ClO_4. All complexes are six-coordinated with O_h symmetry.

Key Words: Cr(III), Mn(III), Complexes, Hydrazone.

INTRODUCTION

The medicinal, analytical and synthetic applications of pyrazolone derivatives are well known[1, 2]. Pyrazolone derivatives are also known to form hydrazones which show varied ligational behaviour towards metal ions in addition to their high physiological activity[3]. Though there are many reports of metal complexes of such hydrazones, only a few attempts have been made to synthesize the complexes of hydrazones obtained by the diazo coupling of aminopyrazolones with the reactive methylene group of β-dicarbonyl compounds. Author's recent reports have shown the formation of one such hydrazone 1,2-dihydro-1-phenyl-2,3-dimethyl-4-[2′,4′-pentanedione-3′-hydrazono]pyrazol-5-one (AAPAAC), prepared by the coupling of diazotised aminoantipyrine with acetylacetone[4]. This compound was found to retain its hydrogen bonded hydrazone form (Fig. 1) when complexed with iron(III).

This paper presents the ligational behaviour of AAPAAC toward chromium(III) and manganese(III) ions.

EXPERIMENTAL

4-Amino antipyrine (Fluka) and acetylacetone (Sisco Chem) were used as received for the synthesis of AAPAAC. All other reagents used were of AR grade.

The metal content in the complexes was determined by standard methods. The C, H, N contents of the ligand and complexes were estimated by microanalysis. Chloride and bromide in the complexes were estimated by Volhard's method, perchlorate by Kurtz method and nitrate was determined using nitron reagent[5, 6]. The molar conductance values of the complexes were measured at room temperature on Systronics direct reading conductivity meter-304 having a cell constant of

1.30 cm^{-1}. Magnetic susceptibilities of the complexes were measured at room temperature on a Gouy balance using $Hg[Co(NCS)_4]$ as a standard. The IR spectra of the ligand and the complexes were recorded in the range 4000–400 cm^{-1} on a Perkin-Elmer 397 IR spectrophotometer using KBr discs. UV-Vis spectra were recorded on a Cary 2390 UV-Vis-NIR spectrophotometer using methanol as solvent. The TG curves of the complexes were obtained on a Shimadzu DT-40 thermal analyzer in air at the rate of 10°C/min.

Synthesis of ligand

The ligand was prepared by coupling diazotized 4-aminoantipyrine (10.15 g, 50 mmol) with acetylacetone (6 mL, 60 mmol) as reported earlier using $NaNO_2$ (5 g, 72 mmol) and HCl[4]. The bright shining yellow crystals of the ligand isolated were characterized by elemental analysis, IR, ^1H and ^{13}C NMR and mass spectral studies[4].

Preparation of the complexes

The complexes were prepared by a general method by refluxing methanolic solutions of the metal salt (0.01 mol) and ligand (30 mmol) in methanol for 3 h. The solid complexes which separated on concentrating the reaction mixture were filtered, washed several times with hot benzene and dried over phosphorous(V) oxide.

RESULTS AND DISCUSSION

Analytical data of the complexes are in agreement with the molecular formulae of the complexes shown in Table-1. The molar conductance data reveal that all the chromium(III) complexes are 1 : 1 electrolytes whereas the chloro and bromo complexes of manganese(III) are 1 : 3 electrolytes and the nitrato and perchlorato complexes are non-electrolytes in the solvents studied.

The IR, ^1H and ^{13}C NMR and mass spectral studies of AAPAAC have revealed an intramolecularly hydrogen-bonded hydrazone structure (Fig. 1) for AAPAAC[4]. The IR spectrum of AAPAAC is characterized by the presence of strong bands at 1720 and 1662 cm^{-1} due to the ν(C═O) of the free acetyl group and pyrazolone ring respectively. The band at 1630 cm^{-1} is assigned to the ν(C═O) of the hydrogen bonded acetyl group. (C═N) is observed as a sharp band at 1617 cm^{-1}. The presence of intramolecularly hydrogen bonded N—H is confirmed[4] by the presence of a weak broad band in the region at 3317 cm^{-1}.

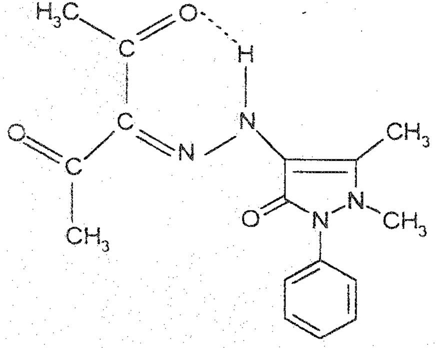

Fig. 1. The structure of AAPAAC

TABLE-1
CHARACTERISATION DATA OF THE COMPLEXES

Complex	Yield (%)	Decomp. temp.	Found (Calcd.), %					Λ_M (Ω^{-1} cm^2 mol^{-1})	μ_{eff} (BM)
			Metal	Anion	C	H	N		
[CrL$_2$Cl$_2$]Cl	75	210	6.52	13.48	48.50	4.51	14.04	18.26	3.82
(Green)			(6.61)	(13.54)	(48.82)	(4.57)	(14.24)		
[CrL$_2$Br$_2$]Br	74	215	5.58	25.99	41.20	3.88	12.10	18.44	3.86
(Red)			(5.65)	(26.08)	(41.73)	(3.91)	(12.17)		
[CrL$_2$(NO$_3$)$_2$]	76	225	5.93	21.40	44.28	4.01	17.32	18.10	3.88
NO$_3$ (Green)			(6.00)	(21.47)	(44.34)	(4.15)	(17.78)		
[CrL$_2$(ClO$_4$)$_2$]ClO$_4$	74	220	5.13	33.20	9.04	33.48	11.28	18.30	3.84
(Deep green)			(5.31)	(30.50)	(39.24)	(3.67)	(11.44)		
[MnL$_2$]Cl$_3$	72	310	6.25	13.02	48.30	4.50	14.01	65.09	4.88
(Deep red)			(6.95)	(13.47)	(48.63)	(4.55)	(14.18)		
[MnL$_2$]Br$_3$	71	312	5.65	25.85	41.12	3.54	12.01	68.75	4.91
(Deepred)			(5.95)	(26.00)	(41.60)	(3.90)	(12.13)		
[MnL(NO$_3$)$_3$]	72	330	9.75	33.20	34.30	3.18	17.50	8.30	4.90(
(Deep red)			(9.90)	(33.51)	(34.59)	(3.24)	(17.65)		
[MnL(ClO$_4$)$_3$]	70	325	8.02	44.50	28.52	2.50	8.24	8.20	4.92
(Deep red)			(8.23)	(44.72)	(28.76)	(2.69)	(8.39)		

The ^{1}H NMR spectrum of AAPAAC shows that the chemical shift of the methyl protons of the CH_3CO group involved in the H-bonded system (δ 2.5) is slightly downfield from that of the free acetyl group (δ 2.35). AAPAAC also shows a low-field signal for the hydrazone proton at δ 14.4. The ^{13}C NMR spectrum shows that the acetyl carbonyl signals are at 196.2 ppm (hydrogen-bonded carbonyl) and 195.6 ppm. The carbonyl group of the pyrazolone ring appears at 158.1 ppm and C═N of the hydrazone linkage at 144.1 ppm.

The mass spectrum of AAPAAC is dominated by an intense molecular ion peak M^+ at m/z 314. The appearance of a base peak at m/z 202 indicates that the cleavage occurs at the N—N bond confirming the hydrazone structure of AAPAAC [4].

Comparison of the IR spectra of the chromium(III) complexes with that of the ligand shows a decrease in the ν(C═N) to around 1584 cm^{-1} and the ν(C═O) of the pyrazolone ring to around 1650 cm^{-1} indicating its coordination to the metal atom. In addition to the above changes, it is observed in the manganese(III) complexes that there is a shift in the ν(C═O) of the free acetyl group to around 1672 cm^{-1} indicating its coordination also to the metal atom. In all the complexes there is no shift in the ν(N—H) and ν(C═O) of the H-bonded acetyl group which confirms the formation of the complex without deprotonation[4, 7–9]. Thus AAPAAC acts as neutral bidentate ligand in chromium(III) complexes coordinating with the carbonyl oxygen atom of pyrazolone ring and azomethine nitrogen atom (Fig. 2) and as a neutral tridentote in manganese(III) where, in addition to the above atoms, the oxygen atom of the free acetyl group also takes part in coordination (Fig. 3). Additional bands around 560–530 cm^{-1} and 480–460 cm^{-1} corresponding to M—N and (M—O) stretching vibration support the coordination of N and O atoms to the metal[4].

The unidentate behaviour of nitrate group in both the complexes is revealed by

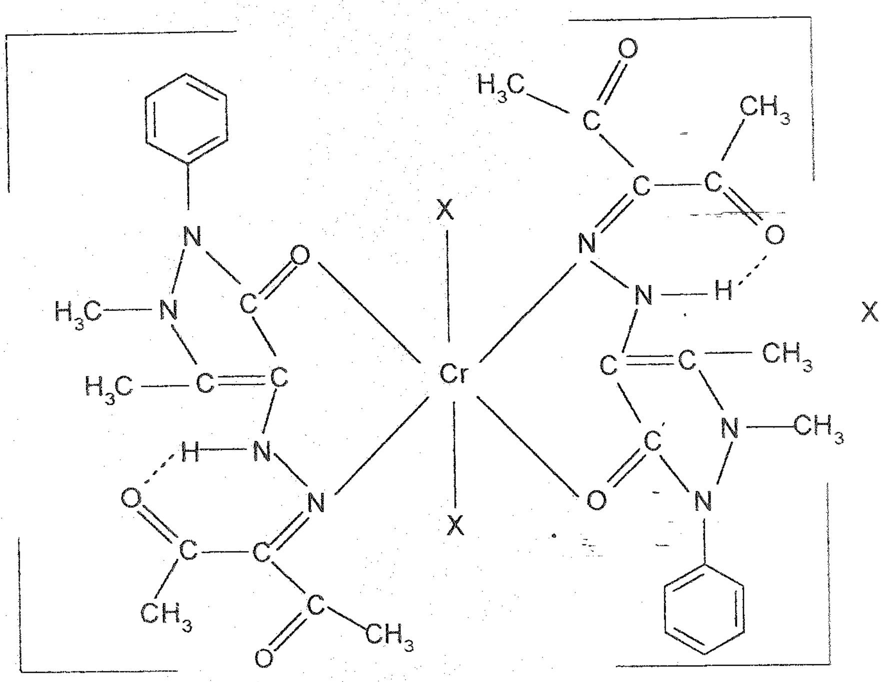

Fig. 2. Structure of $[CrL_2X_2]X$, X = Cl, Br. NO_3, ClO_4

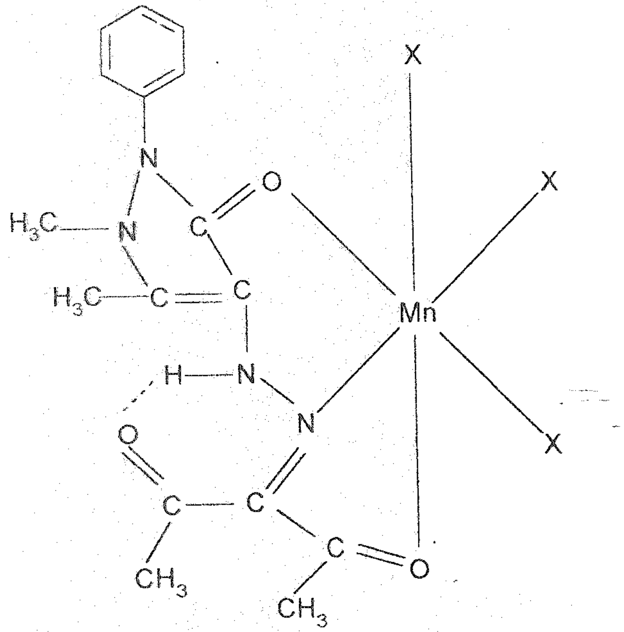

Fig. 3. Structure of $MnLX_3$, X = ONO_2, $OClO_3$

the presence of ν_4 and ν_1 vibrations of coordinated nitrate[4] around 1450 and 1320 cm^{-1}. In addition to these bands, the chromium(III) complex also shows peaks at 1390, 830 and 720 cm^{-1} corresponding to ν_3, ν_2 and ν_4 vibrations of ionic nitrate group[10]. Both the perchlorato complexes have additional bands around 1126 and 1021 cm^{-1} with a weak band at 938 cm^{-1} indicating unidentate coordination of O atom of perchlorate group[4]. Strong bands at 1089 cm^{-1} and 627 cm^{-1} shows the presence of ionic perchlorate group in the chromium(III) complex[10,11]. These observations are supported by conductance measurements also.

The electronic spectra of all the chromium(III) complexes show broad absorption bands at 17500 cm^{-1} and 22700 cm^{-1} assignable to $^4A_{2g} \rightarrow {}^4T_{2g}(F)$ and $^4A_{2g} \rightarrow {}^4T_{1g}(F)$ transitions of octahedral chromium(III). The charge transfer band appearing at 29000cm^{-1} obscures the $^4A_{2g} \rightarrow {}^4T_{2g}(P)$transition[12,13]. Mn(III) complexes show bands around 14700 cm^{-1}, 16600 cm^{-1} and 18500 cm^{-1} assignable to $^5B_{1g} \rightarrow {}^5A_{1g}$, $^5B_{1g} \rightarrow {}^5B_{2g}$ and $^5B_{1g} \rightarrow {}^5E_g$ transitions expected for O_h symmetry[14, 15].

Thermal studies of metal complexes were carried out under static air condition. The thermograms of all the complexes show only a single stage decomposition and it is not of dehydration[3].

The room temperature magnetic moment values of all the chromium(III) complexes show values ranging from 3.82 to 3.88 BM. These values are very close to the spin only value of octahedral chromium(III) complexes[16]. The magnetic moment values of manganese(III) complexes are also in agreement with high spin O_h symmetry around manganese(III)[3].

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