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Chromium (III) Complexes of Esters of Carbazic Acid

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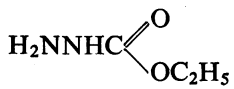
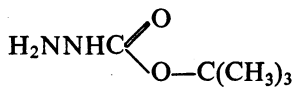
Complexes of ethyl and t-butyl esters of carbazic acid with $CrX_3.nH_2O$ ($X = NO_3^-$, Cl^-, Br^-, I^-, NCS^-) have been prepared and characterized on the basis of vibrational and electronic spectroscopy and magnetic measurements. The bonding occurs through the amino nitrogen and oxygen atom of the ligands. The ligand field parameters have also been calculated.

INTRODUCTION

Srivastava et al.[1–3] and others[4–6] have shown that N-substituted carbazic acids behave as bidentate ligands co-ordinating the metal ion through one of the oxygen atoms of the carboxylate group and one of the nitrogen atoms. Some of the metal complexes isolated from the corresponding sulphur ligands have been found to possess biological activity. Hence it was thought worthwhile to investigate the complexes of ethylcarbazate (A) and t-butylcarbazate (B) with some biological metal ions.



(A)



(B)

In this paper we report the complexes of ethyl and t-butyl esters of carbazic acid with CrX_3 ($X = NO^-_3$, Cl^-, Br^-, I^-, NCS^-).

EXPERIMENTAL

The complexes were prepared by the following general method.

An ethanolic solution of respective chromium (III) salt was mixed with an ethanolic solution of the ligands in 1 : 3 molar ratio. Upon stirring the reaction mixture on a magnetic stirrer for several hours, green coloured crystals gradually separated out, which were filtered, washed with absolute ethanol and finally with dry ether and dried in a vacuum desiccator over phosphorous pentoxide.

Chromium was determined in the complexes by complexometric titration with EDTA using murexide as indieator.[7] Analyses for carbon, hydrogen and nitrogen were performed by micro-analytical methods.

Magnetic measurements were performed on the solid samples with a Guoy balance. $HgCo(SCN)_4$ was used as a calibrant. The visible reflectance spectra of the finely powdered compounds were recorded on a Beckman DK-2 spectrophotometer fitted with a standard reflectance attachment and magnesium oxide in the reference beam.

Infra-red spectra were recorded on a Beckman IR-20 spectrophotometer as a nujol mull or Polychlorotrifluoroethylene in the range 4000–400 cm^{-1}.

RESULTS AND DISCUSSION

The interaction of $CrX_3.nH_2O$ (X = Cl, Br, I, NO_3, NCS) with the ligands, ethyl carbazate (CrEt) and t-butyl carbazate (CzBu), results in the formation of the complexes having a general composition CrL_3X_3. The compounds are microcrystalline and are sparingly soluble in most solvents; only in coordinating solvents such as dimethylsulphoxide, acetonitrile and acetone the solubility is relatively high, but then the dissolution is accompanied by extensive solvolysis. This behaviour prevents recrystallization of the product; purification can be accomplished by means of repeated washing with a non-coordinating solvent. The compounds are fairly stable and can be stored for several months without any apparent change. They do not melt upto 250°C.

The magnetic moments and solid state electronic spectra of the complexes agree with those expected for essentially octahedral stereochemistry. The magnetic moment values lie in the range 3.8 to 4.2 BM as expected for the three unpaired electrons.[8]

Analysis of the electronic spectra of complexes allows us to determine the mode of bonding. Three spin-allowed transitions, in order of increasing energy, $^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)(\nu_1)$, $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)(\nu_2)$ and $^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)(\nu_3)$, are predicted for chromium (III) in an octahedral field. The ν_3 transition, expected to appear at about 31000 cm^{-1}, usually is not observed due to intense charge-transfer bands in the ultraviolet region.

Analysis of the electronic spectra of the chromium (III) complexes reported herein exhibit two major bands in the range 14500–15800 and 19680–22280 cm^{-1} (Table 1) which can be assigned to ν_1 and ν_2 transitions, respectively. The band positions are similar to those reported with other oxygen-nitrogen (ON) donor ligands. The most noticeable feature of ν_1 and ν_2 transitions is that the bands are considerably more intense than usual for the octahedral chromium (III) complexes, which may be due to a high degree of covalency and to the lack of symmetry in the complexes.[9-10]

Since the distortion from octahedral structure is small and because there is a lack of supporting detailed spectral data, the spectra have been analysed in terms of an octahedral model and ligand field parameters,

TABLE 1

ELECTRONIC SPECTRAL BANDS AND CRYSTAL FIELD PARAMETERS (cm^{-1})

Compound	$^4A_{2g}(F) \rightarrow {}^4T_{2g}(F) \rightarrow {}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ calc. (ν_1)	(ν_2)	(ν_3)	Dq	B′	β'
$Cr(CzEt)_3Cl_3$	15875	22220	34925	1587	647	0.628
$Cr(CzEt)_2Br_3$	15200	21280	34440	1520	620	0.601
$Cr(CzEt)_3I_3$	14690	21000	32330	1469	599	0.581
$Cr(CzEt)_3(NO_3)_3$	15550	21739	34210	1555	634	0.615
$Cr(CzEt)_3(NCS)_3$	14505	20007	31911	1450	591	0.573
$Cr(CzBu)_3Cl_3$	15130	21326	33286	1513	617	0.599
$Cr(CzBu)_3Br_3$	14250	18870	31350	1425	582	0.565
$Cr(CzBu)_3I_3$	14100	18520	31020	1410	576	0.559
$Cr(CzBu)_3(NO_3)_3$	14850	20050	32670	1485	606	0.588
$Cr(CzBu)_3(NCS)_3$	13900	18520	30580	1390	567	0.550

Dq and B′, have been calculated which are collected in Table 1. The ν_3 has also been calculated and included in Table 1. Ethylester of carbazic acid complexes have higher values of Dq as compared to t-butylester, which may perhaps be due to steric hindrance caused by the t-butyl group.

The Racah parameter, β', may be calculated by several methods, depending on the transitions energies used, but, since only ν_1 and ν_2 bands have been observed in the complexes reported only one equation fitting the second band has been used to calculate 'β''. The β' values are of the order of 56–65% of the free ion value and this indicates considerable orbital overlap.

The β' values in our complexes are in the range 0.55 to 0.63, which are in close agreement with that of other oxygen and nitrogen donor ligands.[12]

In the IR spectra (Table 2) of the ethyl and t-butyl esters of carbazic acid, the bands due to the asymmetric and symmetric stretching vibrations of the NH_2 group in the hydrazine residue appear at **Ca** 3300 and **Ca** 3200 cm^{-1}, which are shifted to lower frequencies in the complexes. This suggests that this group is involved in co-ordination with the chromium (III) ion.[13–15]

The bands at **Ca** 1630 cm^{-1} and **Ca** 1360 cm^{-1} in CzEt and CzBu have been assigned to the asymmetric and symmetric deformation modes of amino group. While the former band appears to have coupled with

TABLE 2

IR SPECTRAL BANDS (cm^{-1}) AND THEIR ASSIGNMENTS IN CzEt AND CzBu AND THEIR Cr (III) COMPLEXES

Compound	ν (NH) or ν (NH_2)	ν (CO)	ν (N—N)
CzEt	3340 m. 3200 m.	1720 m.	1030 m.
$Cr(CzEt)_3Cl_3$	3200 s	1620 m.	995 mbr.
$Cr(CzEt)_3Br_3$	3220 s	1610 s	995 m.
$Cr(CzEt)_3I_3$	3240 m.	1630 m.	1000 m.
$Cr(CzEt)_3(NO_3)_3$	3200 m.	1600 mbr.	990 mbr.
$Cr(CzEt)_3(NCS)_3$	3220 m.	1610 m	995 mbr.
CzBu	3300 s 3200 msh	1700 s —	1020 m.
$Cr(CzBu)_3Ci_3$	3200 m.	1610 s	980 m.
$Cr(CzBu)_3Br_3$	3220 s	1620 m.	995 m.
$Cr(CzBu)_3I_3$	3200 mbr	1610 s	1000 m.
$Cr(CzBu)_3(NO_3)_3$	3220 s.	1635 m.	980 m.
$Cr(CrBu)_3(NCS)_3$	3200 sbr	1620 s	1000 w.

ν (CO), the latter appears at Ca 1370 cm^{-1} in the chromium complexes. The N—N stretching vibration has been assigned to a band at about 1000 cm^{-1} in the free ligands and their complexes. The slightly broad character of this band and occurrence at lower wave numbers in the complexes may be taken as an evidence for the nitrogen involvement in the bond formation.[5]

The carbonyl stretching frequency provides a very important clue to the elucidation of the structures. This band appears at about 1700 cm^{-1} in CzEt and CzBu. This band appears at about 1600 cm^{-1} in the complexes. The lowering of this frequency in the complexes indicates metal oxygen coordination.

Thus, the ligands CzEt and CzBu act as bidentate coordinating the metal via amino nitrogen and carbonyl oxygen atoms.

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