Chromium(III) Complexes of Imidazole Thiones

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Introduction

The complexes formed between heterocyclic thione molecules and chromium, molybdenum and tungsten appear to fall into two distinct types.

With zero-valent metals, thiomorpholine-3-thione (tmtH) [1], thiazolidine-2-thione (tzdtH) [2] and imidazoline-2-thione ($imtH_2$) together with its N(1)-methyl (mimtH) and N(1), N(3) di-methyl (dmimt) derivatives [3] form complexes of general formula: $M(CO)_5L$. The monodentate sulphur donating character of the ligands has generally been established from the infrared spectra of the complexes by analysis of shifts to the ν(NH) and thioamide bands as well as by X-ray analysis of both $W(CO)_5$(tzdtH) [4] and $W(CO)_5$(tmtH) [5].

In contrast to this behaviour the complexes of trivalent chromium with tzdtH [6], benzoxazoline-2-thione (bzoxtH) [7] and tmtH [6] are formulated: $Cr(LH)_3X_3$ (X = Cl, Br, I); the ligands coordinate by means of their imido (NH) groups in these complexes.

On the basis of these observations tzdtH and tmtH appear to be classically ambidentate. However, mimtH is a monodentate sulphur donor towards soft acids: Mo(0) [3], Cu(I) [8], Pd(II) [11] and Pt(II) [12] as well with borderline acids: Co(II), Zn(II) [9] and Ni(II) [10]. Similar behaviour is observed for imtH with the additional tendency for that molecule to S,N-chelate with Co(II) and Zn(II) in the solid [13]. The di-methyl derivative, dmimt, is of necessity a sulphur donor and complexes are reported with Co(II), Zn(II) [14, 15], Ni(II) [16] and Mo(0) [3].

This report is concerned with the preparation and characterisation of the complexes of imidazolethiones with chromium(III).

Experimental

(a) Preparation of the Complexes

The complexes were all prepared by the same general method. Each ligand (3 mmol) was dissolved in the minimum amount of toluene (*ca.* 50 cm^3) at room temperature. The metal salt, $CrCl_3\cdot 6H_2O$ (1 mmol) was dissolved in the minimum quantity of dry acetone (*ca.* 10 cm^3). These solutions were mixed and a further quantity of toluene (*ca.* 20 cm^3) was added with vigorous stirring. The complexes precipitated rapidly as brown solids and the volume of solution was reduced to *ca.* 15 cm^3 under vacuum. The products were removed by decantation, washed with cold ether and vacuum dried. Yields, 50–60%.

(b) Chemical Analyses

C, H, N and Cr were analysed by Butterworth's Laboratories Ltd., Teddington, Middlesex.

(c) Physical Measurements

Infrared spectra were recorded as mulls and discs (CsI) in the range 4000–200 cm^{-1} on a Perkin-Elmer 577 grating spectrophotometer. Solid state reflectance spectra were recorded on a Unicam SP1700 spectrophotometer in the range 350–850 nm. Solution electronic spectra were recorded on a Cary 17D spectrophotometer in the range 200–2000 nm. Magnetic measurements were recorded at room temperature using a Gouy balance with $Hg[Co(NCS)_4]$ as standard. Molecular susceptibilities were corrected for the diamagnetism of the component atoms.

Results and Discussion

The complexes are listed in Table I together with their elemental analyses as well as other physical and chemical properties. Major infrared bands of the ligands and the complexes are in Table II; Table III contains electronic spectral and relevant spectrochemical data.

The complexes are intensely hygroscopic, which accounts for some deviations between calculated and observed elemental analyses; they are also fairly low

TABLE I. Analytical Data, found % (calcd. %); Room Temperature Magnetic Moments and Melting Points.

Compound	Colour	Cr	C	H	N	μ_B	M.P.
$Cr(imtH)_3Cl_3$	brown	10.6(11.34)	23.6(23.55)	3.0(2.6)	17.6(18.32)	3.5	120
$Cr(mimtH)_3Cl_3$	brown	10.7(10.39)	28.0(28.77)	4.3(3.6)	15.7(16.78)	3.4	133
$Cr(dmimtH)_3Cl_3$	brown	9.5 (9.58)	32.7(33.18)	4.8(4.4)	14.8(15.48)	3.5	145

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TABLE II. Major Infrared Bands of the Complexes with Relevant Bands of the Free Ligand in Brackets.

$Cr(imtH)_3Cl_3$	$Cr(mimtH)_3Cl_3$	$Cr(dmimt)_3Cl_3$	Assignment
3700–2600br,s	3650–2600br,s	3700–2600br,s	ν(OH) ν(NH) ν(CH)
1700w	1620w	1620w	δ(HOH)
1585s(1585s)	1520s(1570s)	1560s(1575s)	ν(C=C) + ν(C=N)
1475s(1480s)	1470s 1450sh (1460s)	1490s(1490s)	THIOAMIDE I
1220vw(1225s)	1285m(1275s)	1240s(1240s)	THIOAMIDE II
1065m(1070m)	1090m(1090m)	1080w(1080w)	THIOAMIDE III
730m (780m) (730s)	740br(770sh,740m)	750m, 730s,(750, 730s)	THIOAMIDE IV
670w(670m)	670m(670m)	660m(660m)	δ(C–S)
500w(520m)	510w(530m)	520m,500br,w(520m)	π(C–S)
300br,m	340m,320s	320m,290m	ν(M–L)

(s, strong; m, medium; w, weak; vw, very weak; br, broad; sh, shoulder).

TABLE III. Electronic Reflectance (and Solution) Spectra (cm^{-1}) with Ligand Field Parameters.

Compound	$^4A_{2g} \rightarrow {}^4T_{2g}$	$^4A_{2g} \rightarrow {}^4T_{1g}(F)$	Dq	B′	β
$Cr(imtH)_3Cl_3$	13966 (13624)	19379 (19608)	1397 (1362)	517 (619)	0.56 (0.67)
$Cr(mimtH)_3Cl_3$	13966 (13333)	19685 (18519)	1397 (1333)	563 (493)	0.61 (0.54)
$Cr(dmimt)_3Cl_3$	13333 (14245)	19157 (20243)	1333 (1425)	606 (593)	0.66 (0.65)

(B for the Cr(III) ion is 918 cm^{-1})

melting and apparently molecular in character which inhibited effective thermal analysis due to their inherent volatility.

The hydrated nature of the complexes is also evident from their infrared spectra which contain a very broad and intense absorption in the range 3700–2600 cm^{-1} together with δ(HOH) between 1620 and 1700 cm^{-1}.

Changes in ν(CN) activity (1460–1585 cm^{-1}) are marginal in the complexes and indicate that the imido (NH) atoms of imtH and mimtH are probably not involved in primary coordinate bond formation; secondary contacts, in the region of 3.0 Å, are possible and in view of their relatively weak nature are not always evident in the infrared spectra of the complexes.

The most significant changes in the infrared spectra of the ligands upon coordination occur in the (CS) region (780–500 cm^{-1}). Both imtH and mimtH have similar activity in this region in the free ligand as well as in the complexes. The thioamide IV bands of both ligands collapse to a single band in the complexes and the remaining two bands (δ(CS), π(CS)) become broader and less intense. The bands of dmimt are the least affected upon coordination; the changes, again in the (CS) region, are limited to a slight broadening and loss of intensity. All three complexes exhibit metal–ligand vibrational activity in the region 290–340 cm^{-1}. Since this region has provided evidence for ν(M–S) activity on previous occasions [9–13, 15] we propose that these bands, coupled with the distinct perturbation in the (C–S) region, strongly suggest sulphur coordination by all three ligands to chromium(III).

The room temperature magnetic moments (Table I) are slightly below those previously observed for chromium(III) complexes of heterocyclic thiones (3.7–4.1 B.M.) [6, 7]. The observed differences are probably due to the hygroscopicity of the complexes but the values nevertheless are indicative of octahedral chromium(III).

The reflectance spectra consist of two bands with ν_1 ($^4A_{2g} \rightarrow {}^4T_{2g}$) in the range 13300 to 1400 cm^{-1} and ν_2 ($^4A_{2g} \rightarrow {}^4T_{1g}(F)$) between 19000 and 19700 cm^{-1} (Table III). A charge transfer band overlaps the ν_2 band and totally obscures the ν_3 band which is expected to occur in the region of 30500 cm^{-1}. Spectrochemical parameters (Dq, B′, β) have been calculated by Tanabe-Sugano procedures [17, 18]. The Dq values place the ligands in the lower end of the spectrochemical series and close to the chloride ion (Dq for $CrCl_6^{3-}$ is 1318 cm^{-1} [17]). The Racah parameters are closer to the range observed for CrN_3X_3 chromophores (β: 0.58–0.65) [6, 7], rather than CoS_6 systems (β: 0.44–0.45) [17], the latter however do appear to involve S–S chelates. However, since $Cr(dmit)_3Cl_3$ is, of necessity, a CrS_3Cl_3 chromophore and since this complex has the largest β value it seems reasonable to presume that the other complexes in this series are also CrS_3Cl_3 chromophores.

The major differences between the reflectance and the solution, (10^{-3} *M*, EtOH), spectra are a clear separation between ν_2 and the charge transfer band and some splitting of the ν_1 band. The latter probably indicates either the commencement of solvolysis or the presence of low symmetry components of the crystal field.

The formation of CrS_3Cl_3 chromophores by the imidazole-thione molecules contrasts sharply with the formation of CrN_3X_3 groups by tmtH [6] bzoxtH [7] and tzdtH [6]. While the acceptor character of the metal may be a factor in deciding the donor behaviour of the latter group of molecules it has not modified the donor character of the imidazole-thiones. These molecules are sulphur donors regardless of the character of the coordinated atom. Consequently, the factors which appear to dominate the donor behaviour of the imidazole-thiones are the molecular and electronic configurations of the molecules together with the reaction media employed.

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