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Mass Spectrometry Data for Tris(dimethyldithiocarbamato)chromium(III) and -indium(III), $Cr(dmtc)_3$ and $In(dmtc)_3$

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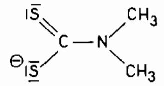
Mass spectrometry data were collected and compared for the interesting tris-dithiocarbamato chelates named in the above title, with the Cr^{III} *complex containing the potential* π*-acceptor* $t_{2g}{}^3$ *subshell and the* In^{III} *complex with its complete shell* $t_{2g}{}^6\ e_g{}^4$*. One part of the comparison shows that the parent ion* $CrL_3{}^+$ *appears in large abundance, but that* $InL_3{}^+$ *is virtually absent. However, the chelate-deficient species* $ML_2{}^+$ *and* ML^+ *were observed for both Cr and In. A brief comparison was also made with similar data for Cr (acac)*$_3$ *of previous work.*

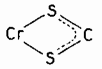
Introduction

In general, inorganic mass spectrometric studies of non-organometallic molecular species appear infrequently in the literature, due usually to low volatilities of such compounds. Furthermore, high temperature spectrometry conditions will often decompose such compounds. Among the conveniently feasible molecules studied to date are the acetylacetonates,[1] for example, with their (MO_6) coordination types. This paper reports on a pair of tris-bidentate chelates which contain the structurally interesting (MS_6) chromaphore, or $Cr(dmtc)_3$ and $In(dmtc)_3$, where $dmtc^-$ symbolizes the dimethyldithiocarbamate anion,



Compounds of this type have been subjected to date to spectroscopic, chemical, structural, and theoretical investigations,[2–5] but their mass spectrometry is unexplored.

We were particularly interested in discovering what behavior differences would appear as a consequence of Cr^{III} having potential π-electron acceptor character ($Cr \leftarrow S$), hence multiple bonding ability due to its half-filled subshell, $t_{2g}{}^3$, whereas In^{III} in $In(dmtc)_3$ has the occupied configuration … $(t_{2g}{}^6)(e_g{}^4)$. For each ML_3 molecule the nature of the electron impact cleavages itself was of interest in view of these rings being four-membered only,



Finally, interesting comparison between $Cr(acac)_3$ with its CrO_6 and $Cr(dmtc)_3$ with its CrS_6 might emerge.

Experimental

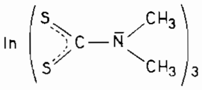
Mass spectra were obtained on an AEI MS–12 instrument using single focusing, 12 inch radius magnetic analyzer, and spectra were recorded on photosensitive paper. The indium complex was prepared in the manner similar to that described by Tomlinson.[2] The chromium compound was prepared as previously described.[4] $InCl_3$ was purchased from Alfa Inorganics, and the ligand Nadmtc was prepared according to the directions of Gleu and Schwab.[6]

Results and Discussion

We give the relative abundancies of observed mass spectrometric peaks of $In(dmtc)_3$ in Table I. Other such data for $Cr(dmtc)_3$ can be found in Table II.

It is immediately obvious from the tables that the $In(dmtc)_3$ parent peak (m/e 475) is virturally absent whereas in the Cr spectrum the molecular ion is present with large intensity (m/e 412). This behavior and the relative magnitudes of normalized abundancies (of *ca.* 71 : 1, *viz.*, normalization of parent peaks over all isotopes to the unity total ion-current) of the two parent peaks lead one to conclude that the (CrS_6) coordination sphere is more strongly bonded than that of (InS_6). This is consistent with better Cr^{III} π-electron acceptor ability, leading to multiple bonding, for accepting sulfur $3p\pi$ electrons into the partially occupied t_{2g} subshell. In addition, these tables show that the abundance of (In^{3+}) is much larger than that of

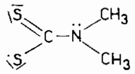
TABLE I. Relative abundancies from



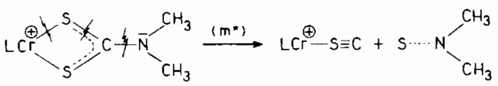
m/e	Ion	Abundance	m/e	Ion	Abundance
475	InL_3^+	0.5	88	$SCN(CH_3)_2^+$	100
387	L_2InS^+	6	73	$SCNCH_3^+$	12
355	L_2In^+	84	72	$SCNCH_2^+$	3
279	$LInSC^+$	16	56	$CN(CH_3)_2^+$	3
235	LIn^+	9	47	SCH_3^+	2
219	m_1* (355→279)		45	$S{-}CH^+$	2
198	m_2* (279→235)		44	$N(CH_3)_2^+$ and SC^+	12
191	InS_2C^+	2			
120	L^+	6	42	$N(CH_3)_2^+$	10
115	In^+	50			

the (Cr^{3+}) free ion, which again is indicative of strong Cr–S bonding relative to In–S. Kinetic and bond stabilities are assumed parallel.

Continuing with $Cr(dmtc)_3$, or CrL_3 (m/e 412), there is a second very prominant peak (m/e 292) and it corresponds to $(CrL_2)^+$. In fact we also observe a metastable peak at m* = 207 which represents process 412→292, or $(CrL_3)^+ \xrightarrow{(m^*)} (CrL_2)^+$, with the other product probably being the neutral ligand molecule

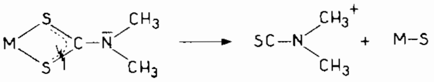


A second metastable peak at m* = 160 corresponds to conversion 292→216, or



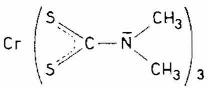
The appearance of this ion product, $LCr^+{-}S{\equiv}C$, is quite interesting since it suggests the possibility of what is probably an S-bonded thiocarbonyl, $Cr{-}S{\equiv}C$, when chromium is in the low (+1) oxidation state, which ought to be electrochemically accessible. Further suggestions for such a possibility is the existance of species Cr^+SC (m/e 96, but at only 4% abundance).

The most abundant cationic ligand fragment is $(SCN(CH_3)_2)^+$ (m/e 88, 100% ab). It is reasonable to suggest part of its origin from



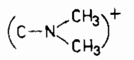
since similar bond breaking steps which create M–S containing moieties could lead to the following observed species entered in Tables I and II: $(L_2CrS)^+$, $(CrS_2)^+$, $(CrS)^+$, and $(LCrS)^+$. Another interesting ligand ion fragment results from having lost both sulfur atoms, i.e.,

TABLE II. Relative abundancies* from



m/e	Ion	Abundance	m/e	Ion	Abundance
412	CrL_3^+	82	157	$CrS_2CNCH_3^+$	4
324	L_2CrS^+	1	146	$Cr(SCH_3)_2^+$	4
298	$LCrS_3(CH_3)_2^+$	2	140	$CrSCN(CH_3)_2^+$	7
292	L_2Cr^+	96	131	$CrS(SCH_3)^+$	4
266	$LCr(SCH_3)_2^+$	11	120	L^+	4
260	$LCrSCN(CH_3)_2^+$	7	116	CrS_2^+	11
			96	$CrSC^+$	4
228	$Cr(SCN(CH_3)_2)_2^+$	7	94	$H_3CSSCH_3^+$	4
216	$LCrSC^+$	37	88	$SCN(CH_3)_2^+$	100
207	m_1* (412→292)		84	CrS^+	4
204	$LCrS^+$	3	73	$SCNCH_3^+$	19
178	$CrS(SCH_3)_2^+$	7	56	$CN(CH_3)_2^+$	11
172	CrL^+	22	52	Cr^+	6
160	m_2* (292→216)		47	SCH_3^+	4
			45	SCH^+	4
			44	$N(CH_3)_2^+$ and SC^+	15
			42	$N(CH_2)_2^+$	22
			32	S^+	7

* At electron energy of 10eV and probe temperature of 170° C.



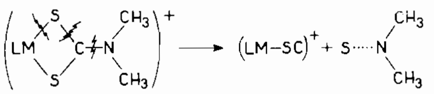
(m/e 56, 11% ab). Even C–N bonds broke so as to result in the formation of $N(CH_2)_2^+$ (m/e 42; 22%).

It is quite interesting as well that the electron impact process caused CrL_3 to end up, in part, as losing none, one, two, and all three ligands, i.e.,

$$\begin{array}{ll} CrL_3 & \xrightarrow[(1)]{e^-} (CrL_3)^+ \\ & \qquad (2)\downarrow \\ & \dashrightarrow_{(3)} (CrL_2)^+ \\ & \dashrightarrow_{(4)} (CrL)^+ \\ & \dashrightarrow_{(5)} (Cr)^+ \end{array}$$

While step (1) and (2) are known to take place, the remainder are open to speculation. Of course step (1) above for the In molecule did not result in a stable molecular ion but the impact produced $(InL_2)^+$ in high abundance at the detector.

There is an important difference in metastable behavior between Cr and In products. While indeed they had a common metastable peak,

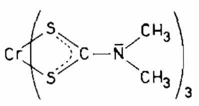


where M = In or Cr, the Cr product fragments (X), are stable but the In ones dissociate further:

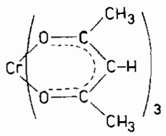
$$(LCr{-}SC)^+ \rightarrow NR$$

$$(LIn{-}SC)^+ \xrightarrow{m^*} (LIn)^+ + SC$$

We conclude by comparing some features of mass spectrum of the presently studied



with that of $Cr(acac)_3$, or



reported by Bancroft, *et al.*[1] One finds that parent ions, CrL_3^+, and ligand-deficient species $(CrL_2)^+$ and $(CrL)^+$ exist for both and that they appear in high abundance. However, the $Cr(acac)_3$ fragmentation pattern had no counterparts to $(LCr{-}SC)^+$ and $(CrS)^+$.

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