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Thermal studies on some metal complexes of hexamethyleniminecarbodithioate

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Abstract

Hexamethyleniminecarbodithioate complexes of the type $M(HMICdt)_n$, where M is a metal, Pb(II), Bi(III), Ti(IV), Se(IV), Th(IV), UO_2(VI) or MoO_2(VI), n is the valency of the metal, and HMICdt is hexamethyleniminecarbodithioate, have been synthesized and characterized. In these complexes, the dithio (CSS^-) group exhibits univalent, bidentate character and coordinates symmetrically with the metal through the bisulfur fork. Thermogravimetric studies indicate that there is an initial endothermic reaction, followed by an exothermic reaction. The heat of volatilization and dissociation were calculated from the TG curves.

INTRODUCTION

Many researchers have been intrigued by the chemistry of the dithiocarbamates of various metals because of their striking structural features and applications in diverse areas [1–4], most notably in rubber technology and agriculture. Numerous biological and biochemical studies [5] have provided further impetus for additional chemical and structural work on these systems. A survey of earlier investigations [6–9] shows that no systematic study has been reported on the hexamethyleniminecarbodithioate complexes of dioxouranium, of dioxomolybdenum or of metals with high coordination number. The present paper describes briefly the synthesis and characterization of these compounds, and presents the thermal studies in more detail.

EXPERIMENTAL

Synthesis

The ligand (sodium hexamethyleniminecarbodithioate dihydrate) NaHMICdt · $2H_2O$ Structure 1 was prepared by the standard method [10]. The

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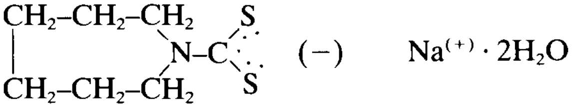
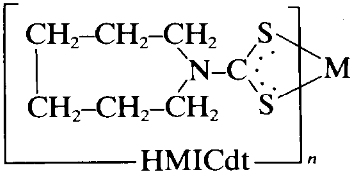


Structure 1. NaHMICdt · $2H_2O$ is sodium hexamethyleniminecarbodithioate dihydrate.



Structure 2. M is Pb(II), Bi(III), Ti(IV), Se(IV), Th(IV), UO_2(VI), MoO_2(VI); n is the valency of the metal ion.

crystallized ligand showed the expected elemental analysis, and IR and ^1H NMR spectra. Thermogravimetric analysis indicated two moles of water of crystallization.

Bis(hexamethyleniminecarbodithioate) lead(II), Pb(HMICdt)$_2$

An aqueous solution of the ligand was added slowly to 100 cm^3 of an aqueous solution (pH 3–3.5) of $Pb(NO_3)_2$ (2 mmol) in 1:2 ratio of metal to ligand. The precipitate formed was filtered, washed with distilled water, and finally with ethanol. It was then dried over P_2O_5 in vacuum. The yield obtained was 80%

Tris(hexamethyleniminecarbodithioate) bismuth(III), Bi(HMICdt)$_3$

An aqueous solution of the ligand (2 mmol) was added to an aqueous solution of $Bi(NO_3)_3$ in 1:3 (M:L) proportion, with constant stirring. The resulting intense yellow precipitate was filtered, washed with distilled water and finally with ethanol, and dried over P_2O_5 in vacuum. The yield obtained was 85%.

Bis(hexamethyleniminecarbodithioate) dioxomolybdenum(VI) and dioxouranium(VI), MoO$_2$(HMICdt)$_2$ and UO$_2$(HMICdt)$_2$

An aqueous alcoholic solution of ammonium molybdate, or uranyl nitrate, was mixed with an aqueous solution of ligand (1:2 ratio) with constant stirring. The molybdate reaction mixture was chilled and acidified with 1 N HNO_3 until the pH was 5.5 and the molybdenal complex obtained. Both complexes were filtered, washed with water and finally with ethanol. They were dried over P_2O_5 in vacuum. The yield obtained was 75%.

Tetrakis(hexamethyleniminecarbodithioate) titanium(IV), selenium(IV) and thorium(IV), Ti(HMICdt)$_4$, Se(HMICdt)$_4$ and Th(HMICdt)$_4$

To an aqueous alcoholic solution of titanium tetrachloride, selenium dioxide or thorium nitrate, was added an aqueous solution of ligand in stoichiometric ratios (1:4 molar), with constant stirring. When the reaction was complete, the alcohol was removed under vacuum at room temperature. The complexes were washed with distilled water and finally with ethanol, and dried over P_2O_5 in vacuum. The yield obtained was 70%.

Instrumentation

All metals were estimated, following decomposition of the complexes with a mixture of concentrated nitric and hydrochloric acid, using a LABTAB-8440MM ICP atomic emission spectrometer (ICP-AES). C, H, N and S analyses were carried out by routine methods, and are recorded in Table 1.

Molar conductance measurements were made in nitrobenzene (1 mM concentration) at room temperature on an Elico digital conductivity meter. Magnetic susceptibilities were recorded on a Faraday magnetometer at room temperature and at several low temperatures. The IR spectra of the complexes and the ligand were recorded in CsI on a Pye Unicam SP-2000 spectrometer in the range 4000–200 cm^{-1}. ^1H NMR spectra of the complexes and ligand were recorded on a VXR-3005 Supercon FT-NMR spectrometer using d_6-DMSO. Electronic spectra in chloroform were recorded on a Shimadzu recording spectrophotometer. Thermogravimetric analyses (TGA and DTA) were carried out in nitrogen on a Shimadzu, DT-30 recording thermal analyzer up to 900°C. A scan rate of 10°C min^{-1} and a chart speed of 2.5 mm min^{-1} were used.

TABLE 1

Characterization of the complexes

Complex and colour	Mol. wt.	ΔM/ $\Omega\,cm^{-1}\,mol^{-1}$	Calc. (found) in %					Magnetic nature
			M	C	H	N	S	
$Pb(HMICdt)_2$	555	0.39	37.29	30.27	4.32	5.04	23.06	
(White)			(37.30)	(30.30)	(4.25)	(5.12)	(23.00)	Diamagnetic
$Bi(HMICdt)_3$	731	0.19	28.59	34.47	4.92	5.74	26.26	
(Intense yellow)			(28.64)	(34.55)	(4.95)	(5.64)	(26.16)	Diamagnetic
$Ti(HMICdt)_4$	744	0.41	6.45	45.16	6.45	7.52	34.40	
(Reddish orange)			(6.37)	(45.26)	(6.36)	(7.40)	(34.20)	Diamagnetic
$Se(HMICdt)_4$	775	0.21	10.19	43.35	6.19	7.22	33.03	
(Orange-red)			(10.26)	(43.10)	(6.00)	(7.05)	(33.00)	Diamagnetic
$Th(HMICdt)_4$	928	0.31	25.00	36.20	5.17	6.03	27.58	
(White)			(24.92)	(36.35)	(5.28)	(6.15)	(27.30)	Diamagnetic
$UO_2(HMICdt)_2$	618	0.46	38.51	27.18	3.88	4.53	20.71	
(Yellow)			(38.46)	(27.05)	(3.98)	(4.49)	(20.68)	Diamagnetic
$MoO_2(HMICdt)_2$	476	0.33	20.16	35.29	5.04	5.88	26.29	
(Greenish yellow)			(20.20)	(35.18)	(5.00)	(5.67)	(26.06)	Diamagnetic

Key: m, multiplet; t, triplet.

RESULTS AND DISCUSSION

The elemental analyses (Table 1) confirm the assigned stoichiometries. All the complexes were found to be non-electrolytic and diamagnetic in nature.

The stereochemistry of the complexes was ascertained from their IR, ^{1}H NMR and electronic spectra. The IR spectra of the ligand and the metal complexes are given in Table 2. All the complexes showed bands assigned to $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$ in the 1495–1472 cm^{-1} range which lie between $\nu(\mathrm{C{=}N})$ and $\nu(\mathrm{C{-}N})$ in the 1690–1640 and 1350–1250 cm^{-1} ranges, respectively. The bands present in the 990–950 cm^{-1} range are attributed to the prevailing contribution of the $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$ bond, indicating that the dithio ligand acts as a bidentate ligand: a doublet in the 1000 ± 70 cm^{-1} region is expected in case of monodentate coordination [4]. This suggests that on complexation, the dithio $(\mathrm{CSS})^-$ group coordinates symmetrically as a univalent, bidentate ligand; this is supported by chemical shifts (δ) in the ^{1}H NMR spectra (Table 3).

The electronic spectra of the complexes in chloroform displayed bands at about 23 and 27 kK, and 29 and 35 kK due to intra-ligand and metal–ligand transitions, respectively, which further confirms that the dithiocarbamate ligand is S–S-bonded to the metal, like a bisulfur fork. An additional band at 40 kK observed in $\mathrm{UO_2(HMICdt)_2}$ and $\mathrm{MoO_2(HMICdt)_2}$ was assigned to typical $\mathrm{UO_2^{2+}}$ and $\mathrm{MoO_2^{2+}}$ moieties. This is in agreement with IR bands at 925 cm^{-1} for terminal (dioxo) metal–oxygen bonds [11–13]. All these data suggest a square-planar structure for $\mathrm{Pb(HMICdt)_2}$, an octahedral structure for $\mathrm{Bi(HMICdt)_3}$, $\mathrm{UO_2(HMICdt)_2}$ and $\mathrm{MoO_2(HMICdt)_2}$, and a dodecahedral structure for $\mathrm{Ti(HMICdt)_4}$, $\mathrm{Se(HMICdt)_4}$ and $\mathrm{Th(HMICdt)_4}$.

TABLE 2

Characteristic IR bands (cm^{-1})

Ligand/complex	ν(C–N)	ν_{asym}(CSS)	ν_{sym}(CSS)	ν(M–S)	ν(O=U=O)	ν(O=Mo=O)
$\mathrm{NaHMICdt\cdot 2H_2O}$	1490 (vs)	958 (vs) 978 (vs)	625 (sm)	–	–	–
$\mathrm{Pb(HMICdt)_2}$	1505 (s)	985 (vs)	620 (sm)	380 (sm)	–	–
$\mathrm{Bi(HMICdt)_3}$	1505 (vs)	985 (m)	630 (sm)	380 (sm)	–	–
$\mathrm{Ti(HMICdt)_4}$	1520 (s)	1005 (m) 985 (sm)	625 (sm)	385 (sm)		
$\mathrm{Se(HMICdt)_4}$	1510 (vs)	1010 (m) 980 (sm)	625 (s)	400 (sm)	–	–
$\mathrm{Th(HMICdt)_4}$	1500 (s)	985 (s)	635 (sm)	385 (sm)	–	–
$\mathrm{UO_2(HMICdt)_2}$	1510 (vs)	980 (sm)	635 (sm)	380 (sm)	925 (vs)	–
$\mathrm{MoO_2(HMICdt)_2}$	1550 (vs)	965 (vs)	640 (sm)	390 (sm)	–	928 (s)

Key: s, strong; vs, very strong; m, medium; sm, small.

TABLE 3

^{1}H NMR chemical shifts (δ) of the complexes in d_6-DMSO using TMS as an internal standard

Ligand/complex	^{1}H		
	α-CH$_2$	β-CH$_2$	γ-CH$_2$
NaHMICdt · 2H$_2$O	4.13 (t)	1.68 (m)	1.43 (m)
Pb(HMICdt)$_2$	3.32 (t)	1.81 (m)	1.51 (m)
Bi(HMICdt)$_3$	3.32 (t)	1.77 (m)	1.57 (m)
Ti(HMICdt)$_4$	3.36 (t)	1.74 (m)	1.56 (m)
Se(HMICdt)$_4$	3.33 (t)	1.79 (m)	1.53 (m)
Th(HMICdt)$_4$	3.34 (t)	1.69 (m)	1.59 (m)
UO$_2$(HMICdt)$_2$	3.34 (t)	1.77 (m)	1.56 (m)
MoO$_2$(HMICdt)$_2$	3.32 (t)	1.82 (m)	1.51 (m)

Key: m, multiplet; t, triplet.

Pb(HMICdt)$_2$

The TG curve of this complex revealed that volatilization started at 240°C and continued to higher temperature; when volatilization was accompanied by simultaneous dissociation; this continued upto 590°C, when the weight of the residue remained unchanged. The DTA curve showed two endothermic peaks with T_{max} values of 166 and 301°C, and one exothermic peak with T_{max} at 438°C.

Bi(HMICdt)$_3$

The TG curve of the Bi(HMICdt)$_3$ complex showed that volatilization started at 200°C. Subsequently, this was accompanied by dissociation which continued to 528°C where the weight of the residue remained fairly unchanged. The DTA curve showed two endothermic peaks with T_{max} values of 170 and 280°C, and one exothermic peak with T_{max} at 488°C.

Ti(HMICdt)$_4$

The TG curve of this complex indicated that the volatilization started at 113°C, followed by dissociation of the complex to 550°C where the weight of the residue remained fairly constant. The DTA curve showed two endothermic and one exothermic peaks, with T_{max} values of 124, 185 and 506°C, respectively.

Se(HMICdt)$_4$

The TG curve of this complex indicated that volatilization started at 175°C. This was followed by dissociation of the complex which continued to

620°C where the weight of the residue remained nearly unchanged. The DTA curve exhibited two endothermic and one sharp exothermic peaks, with T_{max} values of 128, 185 and 478°C, respectively.

Th(HMICdt)$_4$

The TG curve of this complex revealed that volatilization started at 120°C and continued at a rapid rate to 170°C. Thereafter, it continued at a moderate rate, associated with partial dissociation, upto 650°C where the weight of the residue remained virtually unchanged. The DTA curve exhibited one broad but small endothermic peak with a T_{max} value of 149°C, indicating that the reaction was dominated by the rapid volatilization of the complex which obscured the second endothermic peak. The small exothermic peak with a T_{max} of 246°C was due to the partial dissociation of the remaining portion of the complex.

UO$_2$(HMICdt)$_2$

The TG curve of this complex indicated that the volatilization started at 180°C, followed by the dissociation of the complex which continued upto 550°C, where the weight of the residue remained unchanged. The DTA curve exhibited two endothermic and one exothermic peaks, with T_{max} values of 104, 193 and 521°C, respectively.

MoO$_2$(HMICdt)$_2$

The TG curve of this complex showed that the volatilization started at 190°C. This was dominated by simultaneous dissociation of the complex which continued to 550°C where the weight of the residue remained fairly unchanged. The DTA curve exhibited one endothermic and two exothermic peaks with T_{max} values of 155, 353 and 450°C, respectively. The second endothermic peak was masked by the simultaneous dissociation of the complex, resulting in an exothermic peak. The second exothermic peak was perhaps mainly due to partial dissociation of the remaining portion of the complex.

The results of the TG and DTA studies and the volatilization patterns are presented in Tables 4 and 5. The TG curves are given in Fig. 1 and DTA curves are presented in Fig. 2. For all the complexes, the DTA curves contain two endothermic peaks. The first endothermic peak is perhaps the

TABLE 4

Thermal analysis

Complex	TG		DTA		
	Temperature range of volatilization/°C	Thermal effect	T_{max}/°C	Heat of volatilization ΔH_1/kcal mol^{-1}	Heat of dissociation ΔH_2/kcal mol^{-1}
$Pb(HMICdt)_2$	–	Endothermic	165		
	240–310	Endothermic	301	+305	−422
	325–590	Exothermic	438		
$Bi(HMICdt)_3$	–	Endothermic	170		
	200–320	Endothermic	280	+343	−532
	340–520	Exothermic	488		
$Ti(HMICdt)_4$	113–165	Endothermic	124		
	173–260	Endothermic	185	+229	−457
	380–550	Exothermic	506		
$Se(HMICdt)_4$	–	Endothermic	128		
	175–240	Endothermic	185	+425	−525
	390–620	Exothermic	478		
$Th(HMICdt)_4$	–	–	–		
	120–190	Endothermic	149	+305	−433
	210–650	Exothermic	246		
$UO_2(HMICdt)_2$	–	Endothermic	104		
	180–270	Endothermic	193	+114	−122
	400–550	Exothermic	521		
$MoO_2(HMICdt)_2$	–	Endothermic	155		
	200–300	Exothermic	353	−262	−327
	300–550	Exothermic	450		

TABLE 5

Thermal dissociation data

Complex	Step I		Step II	
	Temp. range of volatilization/°C	Observed (calculated) weight losses in %	Temp. range of dissociation/°C	Observed (calculated) weight losses in %
$Pb(HMICdt)_2$	240–310	24.86 (24.32)	325–590	32.06 (31.40)
$Bi(HMICdt)_3$	200–320	57.04 (58.12)	340–520	9.91 (8.24)
$Ti(HMICdt)_4$	113–400	79.00 (78.10)	430–550	6.10 (6.51)
$Se(HMICdt)_4$	175–480	62.15 (62.50)	500–620	18.25 (17.80)
$Th(HMICdt)_4$	120–190	52.37 (51.68)	210–650	15.73 (16.12)
$UO_2(HMICdt)_2$	180–270	40.58 (39.32)	400–550	16.53 (16.92)
$MoO_2(HMICdt)_2$	190–300	28.89 (29.47)	300–550	44.11 (43.62)

result of some volatilization of the metal chelate. The second endothermic peak is caused by the volatilization of the complex itself, while the third exothermic peak is due to partial dissociation [14] of the remaining portion of the complex. No additional peaks are observed.

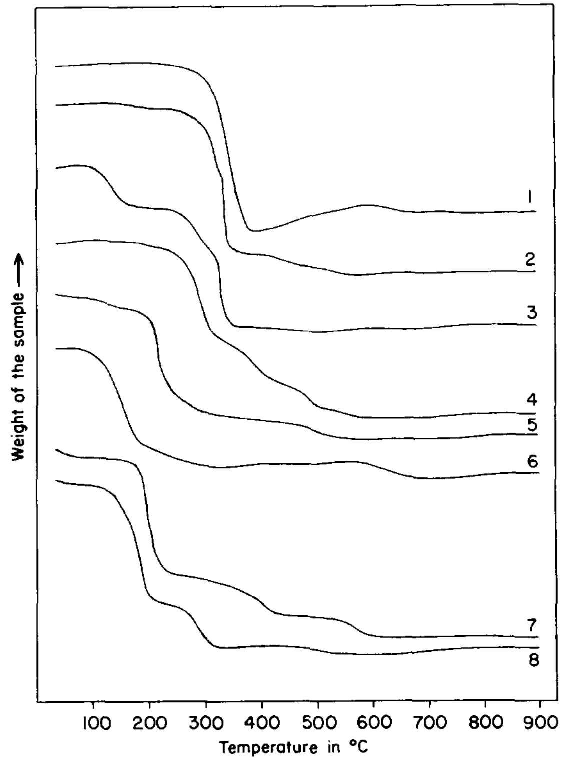


Fig. 1. TG: 1, $Pb(HMICdt)_2$; 2, $Bi(HMICdt)_3$; 3, $NaHMICdt \cdot 2H_2O$; 4, $MoO_2(HMICdt)_2$; 5, $UO_2(HMICdt)_2$; 6, $Th(HMICdt)_4$; 7, $Se(HMICdt)_4$; 8, $Ti(HMICdt)_4$.

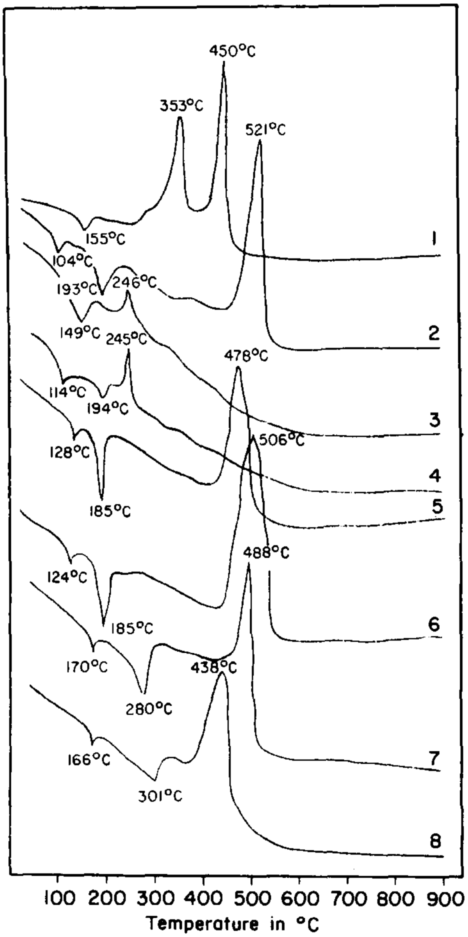
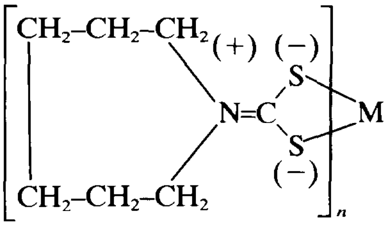


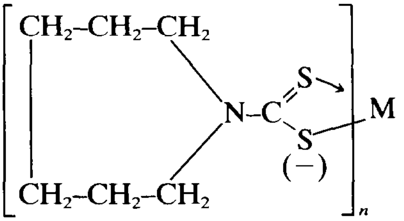
Fig. 2. DTA: 1, $MoO_2(HMICdt)_2$; 2, $UO_2(HMICdt)_2$; 3, $Th(HMICdt)_4$; 4, $NaHMICdt \cdot 2H_2O$; 5, $Se(HMICdt)_4$; 6, $Ti(HMICdt)_4$; 7, $Bi(HMICdt)_3$; 8, $Pb(HMICdt)_2$.

The volatility of these complexes may be explained by reference to their sturctures. According to Moshier and Siever [15], these complexes showed the absence of localized structures and the presence of π-bonding between the chelating agent and the metal. Hence, these complexes would be expected to volatilize at relatively low temperatures. However, the partial dissociation of these complexes at higher temperatures may be due to the presence of secondary structures [14, 16] such as Structures 3 and 4.

From the TG curves, the heat of volatilization ΔH_1 and the heat of dissociation ΔH_2, were calculated for the second and third thermal effects for each complex: the first peak (first thermal effect) corresponds to a slight volatilization of the metal chelate. These calculations are based on the equation of Stepin et al. [17]; the values are given in Table 4.



Structure 3. M is the metal ion; *n* is the valency of the metal.



Structure 4. M is the metal ion; *n* is the valency of the metal.

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