Thermochimica Acta, 56 (1982) 241–245
Elsevier Scientific Publishing Company, Amsterdam—Printed in The Netherlands

Note

MASS SPECTRAL AND THERMOGRAVIMETRIC STUDIES OF MOLYBDENUM DITHIOCARBAMATES

M.R. UDUPA and K.S. NAGARAJA

Department of Chemistry, Indian Institute of Technology, Madras-600 036 (India)

(Received 5 January 1982)

Molybdenum forms complexes [1] with the dithiocarbamate ligand in almost all oxidation states from 0 to 6. The number of ligand molecules per molybdenum is found to be a maximum of two in the complexes, with the ligand acting as a bidentate chelate. The remaining positions of the molybdenum polyhedra are occupied by ligands such as O^{2-}, S^{2-}, NO^+, NCS^-, etc. The valence-change concept [2] was proposed to rationalize novel features of the mass spectra of metal complexes as it was observed that the modes of ion dissociation are markedly dependent on the oxidation states usually assumed by the metal atom. Casey et al. [3] have studied the mass spectrum of $Mo_2O_3[(C_2H_5)_2NCS_2]_2$ and confirmed the binuclear nature of the complex. Reported in this note are the mass spectral studies of diethyldithiocarbamates of dinitrosyl molybdenum $[Mo(NO)_2(Et_2NCS_2)_2]$, I, oxoisothiocyanatomolybdenum $[MoO(NCS)(Et_2NCS_2)_2]$, II, and the dimeric disulfidomolybdenum $[MoS_2(Et_2NCS_2)_2]_2$, III. The results of the thermal decomposition of the complexes in air following thermogravimetry are also included.

EXPERIMENTAL

Complexes I, II and III were prepared following the reported methods with suitable modifications [4] for better yields. The mass spectra of the complexes were taken on a VG micromass 70–70 FF double focusing mass spectrometer with a VG 2235 data system. The thermal decomposition was carried out on a Stanton recording thermobalance in air at a continuous heating rate of 6°C min^{-1}.

RESULTS AND DISCUSSION

Molybdenum has seven naturally occurring isotopes spanning from 92–100 mass number units. The binuclear molybdenum fragments consist of 15

0040-6031/82/0000–0000/$02.75

TABLE I

Mass spectral data of molybdenum dithiocarbamates

A. Peaks containing molybdenum

m/e	m^+
I. $Mo(NO)_2(Et_2NCS_2)_2$	
448–456	$Mo(NO)_2(Et_2NCS_2)_2$
418–426	$Mo(NO)(Et_2NCS_2)_2$
388–396	$Mo(Et_2NCS_2)_2$
304–312	$Mo(Me_2NCS_2)(H_2NCS)$, $Mo(EtNHCS_2)(H_2NCS_2)$
270–280	$MoS_2(NCS)_2$, $Mo(Me_2NCS_2)(H_2NCS)$, $Mo(EtNHCS_2)(H_2NCS)$
248–256	$MoS_3(NO)_2$
244–252	$Mo(H_2NCS_2)(NH_2CS)$
218–226	$MoS_3(NO)$
216–224	$MoS_2(NO)_2$
214–222	$Mo(SCHNH_2)_2$
188–196	MoS_3
186–194	$MoS_2(NO)$
183–191	$MoS(SCNH)$
156–164	MoS_2
II. $MoO(NCS)(Et_2NCS_2)_2$	
560–577	$Mo_2O(Et_2NCS_2)_2S_2$
404–412	$MoO(Et_2NCS_2)_2$
198–206	$Mo(MeNHCS_2)$
166–174	$Mo(MeNHCS)$
III. $Mo_2S_4(Et_2NCS_2)_2$	
576–592	$Mo_2S_3(Et_2NCS_2)_2$

B. Peaks due to the diethyldithiocarbamate moiety

m/e	m^+
148	$(C_2H_5)_2NCS_2$
116	$(C_2H_5)_2NCS$
102	$(C_2H_5)CH_3NCS$
88	$(CH_3)_2NCS$, $(C_2H_5)NHCS$
72	H_2CNCS
60	H_2NCS
59	HNCS
58	NCS
44	CS
32	S
30	C_2H_6
29	C_2H_5
28	C_2H_4
27	C_2H_3

closely arranged peaks with distinctive ratios to one another which envelop 17 mass number units. The mass spectral results of compounds I, II and III containing Mo fragments are given in Table 1A and those of the dithiocarbamate ligand moiety are given in Table 1B. The data suggest that the fragmentation of dinitrosyl dithiocarbamate takes place through the stepwise removal of NO, followed by the successive loss of CH_2 groups and S, to give the final molybdenum fragmentation MoS_2 which could also be visualized as the result of the fragmentation of $MoS_3(NO)_2$ obtained by the loss of the organic moiety. There is no indication of the formation of dinuclear molybdenum species as is evident from the absence of 15-line patterns. However, there are several closely spaced peaks clustering between 183–196, 214–226 and 244–256 mass number units. These groups of lines could be analyzed on the basis of the relative abundance of Mo isotopes. Thus, the lines between 183 and 196 consist of three fragmentations, *m/e* 183–191 MoS(SCNH), 186–194 $MoS_2(NO)$ and 188–196 MoS_3. The group of lines between 214 and 226 could be assigned to 214–222 $MoS(SCHNH_2)_2$, 216–224 $MoS_2(NO)_2$ and 218–226 $MoS_3(NO)$. Similarly, the lines between 244 and 256 consist of peaks due to $Mo(H_2NCS)_2(H_2NCS)$ and 248–256, 244–252 $MoS_3(NO)_2$.

The mass spectrum of oxoisothiocyanatobis(dithiocarbamato)molybdenum does not give a parent molecular ion. The 15-line pattern fragmentation at *m/e* 560–577 is attributed to the dinuclear species $Mo_2O(Et_2NCS_2)_2S_2$, which loses the MoS_2 group and finally becomes Mo(MeNHCS).

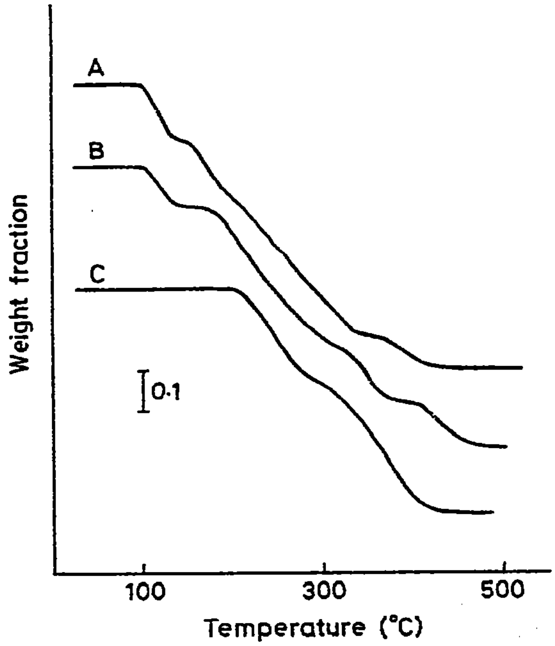

Fig. 1. TG curves of molybdenum dithiocarbamates.

TABLE 2

TG data of molybdenum dithiocarbamates

Compound	Temp. range (°C)	Wt. loss (%)		Probable phase
		Found	Calcd.	
I	100–150	13.0	13.3	$Mo(Et_2NCS_2)_2$
	200–400	57.0	57.5	MoS_3
	420–490	68.0	68.2	MoO_3
II	100–150	12.0	12.5	$MoO(Et_2NCS_2)_2$
	200–420	58.0	58.8	MoS_2
	430–500	31.0	30.9	MoO_3
III	200–300	27.0	27.3	'Mo_2S_8'
	300–450	53.0	53.2	MoO_3

Complex III does not exhibit fragmentation at mass numbers higher than 576–592 for which the parent molecular ion would cover the mass numbers 608–624, probably due to non-volatility of the parent complex. Similar observations were made [3] in the spectrum of $Mo_2O_3(Et_2NCS_2)_2$. The other fragments of Mo peaks are very weak and could not be detected under the experimental conditions.

The fragmentations of the dithiocarbamate moiety are similar in all the complexes. Thus, the ligand $(C_2H_5)_2NCS_2$, *m/e* 148, loses a S atom followed by the stepwise dissociation of CH_2 groups to give NCS.

TG plots of the three dithiocarbamates are given in Fig. 1 and the data are summarized in Table 2. On thermal decomposition in air the S-containing molybdenum compounds give rise to MoO_3 through the intermediate molybdenum sulfides [5–7]. The weight-loss curve indicates that the nitrosyl complex loses two molecules of NO in the temperature range 100–150°C and MoO_3 is formed at 480°C through the intermediate MoS_3. The oxoisothiocyanate complex on the other hand loses NCS in the temperature range 100–150°C. At higher temperature MoS_3 is formed which is oxidized to MoO_3 at about 500°C. Complex III is stable up to 200°C and decomposes to give a polysulfide of composition Mo_2S_8 between 200 and 300°C. The sulfide is oxidized to MoO_3 at about 480°C.

REFERENCES

1 E.I. Stiefel, Prog. Inorg. Chem., 22 (1977) 1.

2 I.S. Shannon and J.M. Swan, Chem. Commun., (1965) 33.

3 A.T. Casey, D.J. MacKey, R.L. Martin and A.H. White, Aust. J. Chem., 25 (1972) 477.

4 K.S. Nagaraja, Ph.D. Thesis, Indian Institute of Technology, Madras, India, 1982.
5 E.Ya. Rode and B.A. Lebedev, Russ. J. Inorg. Chem., 6 (1961) 608.
6 A. Müller, T.P. Prasad and R. Menge, Z. Anorg. Allg. Chem., 391 (1972) 107.
7 T.P. Prasad, E. Diemann and A. Müller, J. Inorg. Nucl. Chem., 35 (1973) 1895.