

THERMOGRAVIMETRIC BEHAVIOUR AND STRUCTURE OF SOME DITHIOCARBAMATES

YU. S. LYALIKOV and M. I. KITOVSKAYA

*Laboratory of Analytical Chemistry, Chemical Institute of the Academy of Sciences
of the Moldavian SSR, Kishinev, USSR*

(Received June 29, 1973)

The study of the thermogravimetric behaviour of different groups of dithiocarbamates and data on the mechanism of their thermal decomposition indicated a formula consisting of dimeric structural units for ethylene-bis-dithiocarbamates of cyclic structure. The dimeric structure concept is in good agreement with experimental data, explains the different behaviours of alkyl- and some alkylenedithiocarbamates, and also yields an explanation for the experimental finding that in the first step of thermal decomposition of the ethylene-bis-dithiocarbamates of divalent metals, one CS_2 group per molecule is set free.

In our previous papers we have demonstrated the difference in thermal behaviour of various groups of dithiocarbamates. Thermal degradation in ethylene-bis-dithiocarbamates of divalent metals starts below 200° and proceeds stepwise. Peaks on the DTA and DTG curves correspond to individual steps on the TG

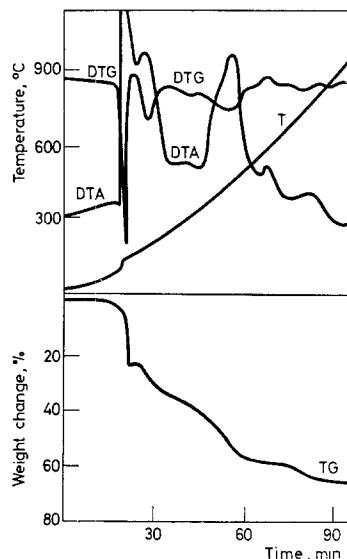


Fig. 1. TG, DTG and DTA curves of zinc ethylene-bis-dithiocarbamate

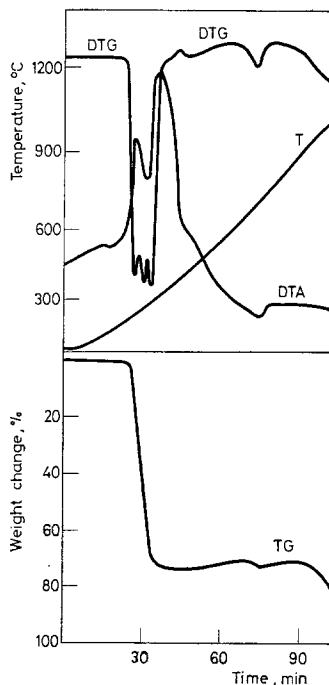
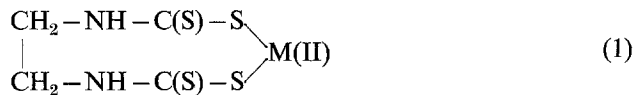
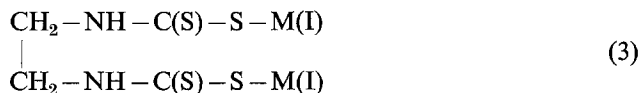
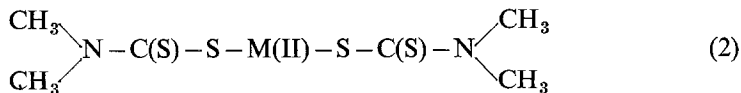


Fig. 2. TG, DTG and DTA curves of iron dimethyldithiocarbamate

curve. Thermal degradation in dimethyldithiocarbamates starts about 100° higher, and is recorded on the TG curve as a single continuous step (Figs 1 and 2). Ethylene-bis-dithiocarbamates of divalent metals were assumed to correspond to the cyclic formula

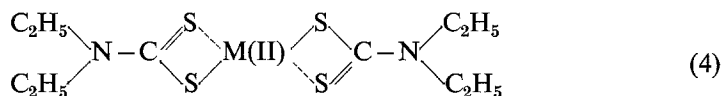


Dimethyldithiocarbamates of divalent metals and ethylene-bis-dithiocarbamates of monovalent metals may be considered open-chain compounds:



It was concluded that the stepwise thermal degradation reflected in the stepwise course of the thermogravimetric curve is specific for ethylene-bis-dithiocarbamates of divalent metals only, and is connected with their cyclic structure [1, 2].

The structures of the dithiocarbamates have not yet been fully elucidated. Reports in the literature on this subject are scarce. Bonamico et al. studied the structures of copper and zinc diethyldithiocarbamates, corresponding to the general formula



by X-ray analysis. They found that in the crystalline state, two centrosymmetrical metal atoms, together with some of the sulphur atoms, form a dimeric structural unit in which each metal atom is coordinated to five sulphur atoms: four sulphur

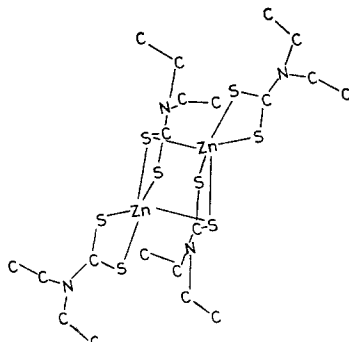


Fig. 3. Structure of zinc diethyldithiocarbamate

atoms as in the monomer molecule, and one sulphur atom of the second molecule arranged centrosymmetrically. The coordination geometry with the metal is close to that of a tetragonal pyramid. In the zinc salt, distortion of the geometry is somewhat greater than in the copper salt. The ligands are planar, with the exception of the extreme CH_3 groups. The central metal atom forms four-membered cyclic chelates with the ligands (Fig. 3). The authors cited also calculated the values of the crystal parameters. These were found to be close to each other for the two compounds studied. In solution (solvents: petrol, chloroform) the dimeric structure is destroyed and the molecular weight of the compounds is normal [3, 4].

Hatfield et al. [5] made use of mass spectroscopy to study zinc diethyldithiocarbamate. They demonstrated that the dimeric structure can also exist in the gas phase. They could not, however, detect molecular dimers in the gas phase, but only dimer splinters.

Pilbrow et al. [6] studied copper(II) coordination compounds with several thioligands by electron paramagnetic resonance. In their opinion, it can be

assumed from EPR spectra that with S-carboxy-diethyldithiocarbamic acid copper forms a chelate whose dimeric form continues to exist in dimethylformamide solution at ambient temperature.

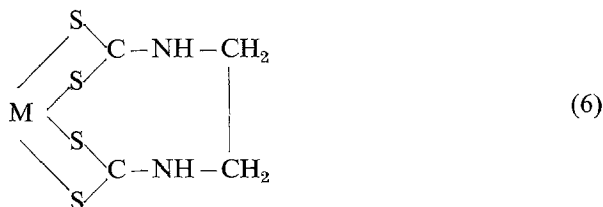
Golding et al. [7] utilized NMR to study a number of iron(III) dithiocarbamates of the type $\left[\begin{array}{c} \text{R} \\ \diagdown \\ \text{N} - \text{C} \begin{array}{l} \diagup \text{S} \\ \diagdown \text{S} \end{array} \\ \diagup \\ \text{R}_1 \end{array} \right]_3 \text{Fe}$, where R and R₁ were aliphatic and cyclic groups. They also found that the iron ion forms four-membered cyclic chelates with the dithiocarbamate anion. They suggested the formula



The compounds studied in the papers cited belong to the group that we termed open-chain dithiocarbamates. Similar studies concerning the structure of cyclic ethylene-bis-dithiocarbamates have not been carried out, possibly because of the difficulties encountered in the separation of the individual compounds for study.

Our own attempts in this direction were also unsuccessful. We did not succeed in preparing or separating individual compounds. Their synthesis is accompanied by substantial amounts of impurities. Purification by means of recrystallization is not feasible, since these compounds do not crystallize from non-complex solvents. Nonetheless, we have made an attempt to elucidate the cause of the differing behaviours in thermal analysis of the two groups of dithiocarbamates, by means of a discussion of other studies in relation to our own results.

According to the formulae suggested in [7], in trivalent iron dithiocarbamates three dithiocarbamate anions are coordinated to the iron atom. Obviously, three groups bound to the metal in chelate rings are capable of free arrangement in space around the central iron atom, choosing the energetically most favourable position and thereby forming a stable structure. The same appears valid for the copper and zinc diethyldithiocarbamates studies in [3] and [4]. If we now assume that in ethylene-bis-dithiocarbamates of divalent metals, the metal atom is bound to the ligand in an analogous manner, such complexes should have the form



In contrast to the previous compounds, in this case not two anions, but one anion with two dithiocarbamate groups is coordinated to the divalent metal atom. In such structures, the free arrangement of the chelate rings relative to the central

metal atom is hindered by the cyclic structure of the ligand. Hence, in this case it is impossible to form structures as favourable energetically as in the case of open-chain dithiocarbamates. If this is true, the thermal stabilities of these compounds must be lower than those of open-chain dithiocarbamates. This expected property was in fact detected in thermal observations: the decomposition temperatures of ethylene-bis-dithiocarbamates of divalent metals are substantially lower than those of all open-chain dithiocarbamates that we have tested.

Further, X-ray analysis of zinc diethyldithiocarbamate [3] demonstrated that in the dimolecular representation, the monomolecules in the dimer are arranged around the centrosymmetrical zinc atom at an angle of about 180° to each other. Calculations of distances and angles in the coordination sphere indicated that one of the Zn-S distances in the intrachelate is substantially longer (by 0.4 \AA) than the Zn-S bond in the interchelate, and also noticeably longer than the other Zn-S bonds in the intrachelate. In other words, two similar ligands behave differently in one and the same monomolecule of the complex. One of the ligands, namely that which is coordinated only to the central zinc atom, exhibits normal Zn-S bond lengths. In the second ligand, which is coordinated to two centrosymmetrical zinc atoms, the lengths of the Zn-S bonds are distorted. The interchelate bond is formed by these second ligands of each monomolecule.

By taking these results into account, we arrived at the following concept. The different coordinations of two ligands of one monomolecule with the metal atoms leads to the non-equivalence of the two chelate rings in the complex. Consequently, the C-S bonds in the rings will also differ in the two ligands; both bond lengths and angles will differ, and thus one dithiocarbamate molecule will contain two non-equivalent CS_2 groups. Such a non-equivalence of the chelate rings and CS_2 groups should be manifested experimentally. A derivatographic analysis of open-chain dithiocarbamates did not reveal differences in behaviour of the two ligands. This, however, is not a convincing proof for the non-existence of different behaviour. It appears more probable that we could not detect the effect, owing to the insufficient sensitivity of the method, since the thermal effects corresponding to the two ligands are located within a narrow temperature range and do not appear articulately on the TG curve. Certain peaks observed on the DTG and DTA curves in the corresponding temperature ranges might be evidence as to the non-simultaneous destruction of the two ligands in the complex. Such data, however, are too few to allow definite statements. The peaks in question may, for instance, reflect thermal effects of impurities.

Let us assume that an analogous dimolecular structure exists in ethylene-bis-dithiocarbamates of divalent metals. In this case, the coordination geometry of the sulphur atoms with the metal in the dimeric structural unit must be distorted to a great extent, owing to the cyclic structure of the complex and to the coordination of the metal atom to two dithiocarbamic groups of one and the same ligand. This distortion will, in turn, enhance the non-equivalence of two chelate rings in the monomolecule of such complexes as compared to the chelate rings in open-chain dithiocarbamates.

This enhancing action does, in fact, occur and is manifested experimentally. The gaseous product evolved in the first step of thermal decomposition of ethylene-bis-dithiocarbamates of divalent metals was identified in our experiments [1, 2] as carbon disulphide, its amount corresponding to one CS_2 group per molecule. This experimental finding confirms the non-equivalence of the two chelate rings within one ligand. The less stable chelate ring is destroyed at a temperature lower by 50 to 60° than the decomposition temperature of the second chelate ring. The C–N and S–M(II) bonds are broken and the unstably bound CS_2 group is set free. The decomposition of the second chelate ring follows another mechanism. This breakdown of the complex is manifested on the TG curve in the form of stepwise decomposition.

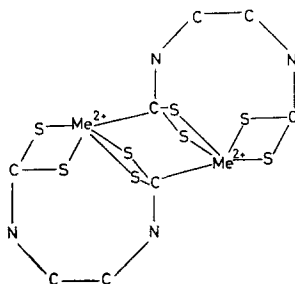


Fig. 4. Dimeric structure of zinc ethylene-bis-dithiocarbamate

These thermal results are in agreement with what is to be expected from the suggested structure of the compound. At the same time, they confirm the assumption that ethylene-bis-dithiocarbamates have a dimeric structure, and that the non-equivalence of the chelate rings and CS_2 groups is enhanced in dithiocarbamates with cyclic ligands as compared to dithiocarbamates with open-chain ligands. This assumption explains the experimental fact that only one CS_2 molecule is evolved per dithiocarbamate molecule in the thermal decomposition of ethylene-bis-dithiocarbamates of divalent metals.

We suggest the formula shown in Fig. 4 for ethylene-bis-dithiocarbamates of divalent metals. The formula represents a dimeric structure in which the monomolecules are connected by M^1-S^2 and M^2-S^1 bonds with greatly distorted geometry of the chelate rings giving rise to the dimeric bond. The agreement of the suggested structure with the experimental data is a convincing proof of its reliability.

References

1. YU. S. LYALIKOV and M. I. KITOVSKAYA, *Ukr. khim. Zh.*, 35 (1969) 719.
2. YU. S. LYALIKOV and M. I. KITOVSKAYA, *J. Thermal Anal.*, 4 (1972) 271.
3. M. BONAMICO, G. MAZZONE, A. VACIAGO and L. ZAMBONELLI, *Acta Cryst.*, 19 (1965) 898.
4. M. BONAMICO, G. DESSY, A. MUGNOLI, A. VACIAGO and L. ZAMBONELLI, *Acta Cryst.*, 19 (1965) 886.
5. J. F. VILLA, M. M. BURSEY and W. E. HATFIELD, *Chem. Comm.*, 7 (1971) 307.
6. J. R. PILBROW, T. D. SMITH and A. D. TOY, *Australian J. Chem.*, 23 (1970) 2287.
7. R. M. GOLDING, W. C. TENNANT, C. R. KANEKAR, R. L. MARTIN and A. H. WHITE, *J. Chem. Phys.*, 45 (1966) 2688.

RÉSUMÉ — L'étude du comportement thermogravimétrique des différents groupes de dithiocarbamates, ainsi que des données sur leur destruction thermique ont permis de proposer une formule qui consiste en unités structurales dimères, pour les bis-dithiocarbamates d'éthylène à structure cyclique. Le concept de la structure dimère, en bon accord avec les données d'expériences, explique le comportement différent des alkyl- et de quelques alkylènedithiocarbamates, et donne aussi une explication du fait établi par voie d'expériences que, lors de la première étape de la destruction thermique des éthylène-bis-dithiocarbamates des métaux bivalents, un groupe CS_2 est libéré par molécule.

ZUSAMMENFASSUNG — Das Studium des thermogravimetrischen Verhaltens verschiedener Gruppen von Dithiocarbamaten und Angaben über die thermische Zerstörung derselben ermöglichten eine aus dimeren Einheiten bestehende Formel für Äthylen-bis-dithiocarbamate mit zyklischer Struktur vorzuschlagen. Das Konzept der Dimerstruktur ist in guter Übereinstimmung mit experimentellen Daten, erklärt das unterschiedliche Verhalten von Alkyl- und einigen Alkylendithiocarbamaten und gibt auch eine Erklärung für den Versuchsbefund, nach dem in der ersten Stufe der thermischen Zerstörung von Äthylen-bis-dithiocarbamaten zweiwertiger Metalle eine CS_2 -Gruppe je Molekül freigesetzt wird.

Резюме — Исследование термогравиметрического поведения отдельных групп дитиокарбаматов и полученные данные о механизме их термической деструкции позволили предложить для этиленбисдитиокарбаматов замкнутого строения формулу в виде димерной единичной структуры. Представление об их димерной структуре хорошо согласуется с экспериментальными данными, объясняет различие в поведении алкил- и некоторых алкилендитиокарбаматов, а также объясняет данные опыта о том, что первым этапом термической деструкции этиленбисдитиокарбаматов двухвалентных металлов является отщепление от молекулы одной группы сероуглерода.