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PREPARATION, CHARACTERIZATION AND THERMAL STUDIES ON BIS-[N-(ETHYL, *m*-TOLYL)-DITHIOCARBAMATO] COMPLEXES OF ZINC(II), CADMIUM(II) AND MERCURY(II)

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Bis-[*N*(ethyl, *m*-tolyl)-dithiocarbamato] complexes of zinc(II), cadmium(II) and mercury(II), abbreviated as $Zn(S_2CNRR')_2$, $Cd(S_2CNRR')_2$ and $Hg(S_2CNRR')_2$, where R is ethyl and R' is *m*-tolyl, have been synthesized. These complexes have been characterized by elemental analyses, molecular weight determinations, conductance measurements and infrared spectral studies. Thermogravimetric studies on the complexes have been carried out in nitrogen and oxygen atmospheres to determine their modes of decomposition.

In recent years, dithiocarbamato complexes have been extensively studied and reports have been well documented on the properties and reactivities of such complexes [1–6]. In the dithiocarbamato complexes of zinc, cadmium and mercury, the metal has the oxidation state +2 and the compounds are of the type $M(R_2dtc)_2$ [2]. However, there is no mention in the literature about four-coordinate complexes of the type, $Zn(S_2CNRR')_2$, $Cd(S_2CNRR')_2$ and $Hg(S_2CNRR')_2$. In these complexes the dithiocarbamate behaves as a bidentate ligand similar to those reported earlier [7]. The thermal properties of these complexes have not been studied either [8–10].

Experimental

All the reactions were carried out in aqueous medium. Sodium *N*-(ethyl, *m*-tolyl)-dithiocarbamate was synthesized by the general method described [11]. *N*-(ethyl, *m*-tolyl)-dithiocarbamato complexes were synthesized by mixing aqueous solutions of the metal sulphate/acetate with the sodium salt of the ligand in 1 : 2 stoichiometric ratio. The white precipitate were washed with distilled water and dried over P_2O_5 under vacuum.

The ligand was estimated by the method of Shankaranarayana and Patel [12]. Zinc, cadmium, and mercury were estimated by standard methods [13]. Nitrogen was estimated by the Kjeldahl method, and sulphur as barium sulphate. Molecular weights were determined in benzene with a Gallenkamp ebulliometer. Conductance measurements were made in nitrobenzene at 30± 0.05° with a Beckmann conductivity bridge, model No. RC-18A. Infrared spectra were recorded in the solid state (KBr pellets) in the region 4000–200 cm^{-1} with a Perkin–Elmer 621 grating spectrophotometer. Thermal studies (TG, DTG) were made on a SETARAM (Lyon, France) G-70 thermobalance (sample size 20–40 mg, heating rate 7°/min, flow rate of gas 10 ml/min).

Results and discussion

The method used for the preparation and isolation of the compounds yielded materials of good purity, as judged by their satisfactory elemental analysis and molecular weight determinations. The elemental analyses (Table 1) indicated a 1 : 2 metal-to-ligand stoichiometry for all the complexes. The complexes are soluble in most of the common organic solvents, particularly in chloroform, acetone and benzene. The molar conductances of 10^{-3} *M* solutions of the complexes in nitrobenzene were found to be 0.30–0.35 ohm^{-1} cm^{2} mole^{-1}, indicating the complexes to be non-electrolytes. From the molecular weight determination of the complexes in benzene, it follows that they are monomeric species. All are stable in air.

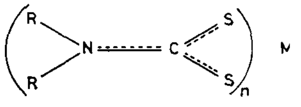
The assignment of various bands in the infrared spectra of metal dithiocarbamato complexes is based on earlier studies [14]. The IR spectra of these compounds possess one medium-intensity band at ~ 1000 cm^{-1}. This indicates the presence of a four-membered ring system, and also supports the bidentate nature of the dithiocarbamate ligand. The thioureide (C . . . N) band near 1500 cm^{-1} is an important characteristic of the dithiocarbamates. The frequency of this band lies between the (C–N) band at 1250–1350 cm^{-1} and the (C=N) bond at 1640–1690 cm^{-1}, suggesting some double bond character. The following general formula

Table 1

Analytical data on the complexes

Complex	Mol. wt.	Percentage of		
		N	S	M
	Found (Calcd.)	Found (Calcd.)		
$Zn(S_2CNRR')_2$	476.00 (485.37)	5.5 (5.7)	26.1 (26.3)	13.1 (13.4)
$Cd(S_2CNRR')_2$	523.00 (532.41)	5.0 (5.2)	23.7 (24.0)	20.9 (21.1)
$Hg(S_2CNRR')_2$	615.00 (620.59)	4.1 (4.5)	20.1 (20.6)	32.0 (32.3)

may therefore be assigned to the compounds:



where *n* is the oxidation state of metal M.

The metal dithiocarbamates showed new bands in the region (400 – 200 cm^{-1}), viz.: ν(Zn – S), 350 w; ν(Cd – S), 345 w; and ν(Hg – S), 340 cm^{-1}.

Thermogravimetric studies

The TG curves of $Zn(S_2CNRR')_2$, $Cd(S_2CNRR')_2$ and $Hg(S_2CNRR')_2$ in nitrogen and oxygen atmospheres (Fig. 1) revealed two steps, and the initial horizontal stretch indicated that the mercury complex was thermally less stable than the zinc and cadmium complexes. In the case of $Zn(S_2CNRR')_2$ and $Cd(S_2CNRR')_2$ in nitrogen atmosphere, the first step corresponded to the formation of their respective thiocyanates, whereas in the case of $Hg(S_2CNRR')_2$ in both atmospheres, it corresponded to the formation of mercuric sulphide, which volatilized off immediately after a small arrest in the TG curve after the first decomposition step. Therefore, in both atmospheres, the second step in the case of the mercury complex was prob-

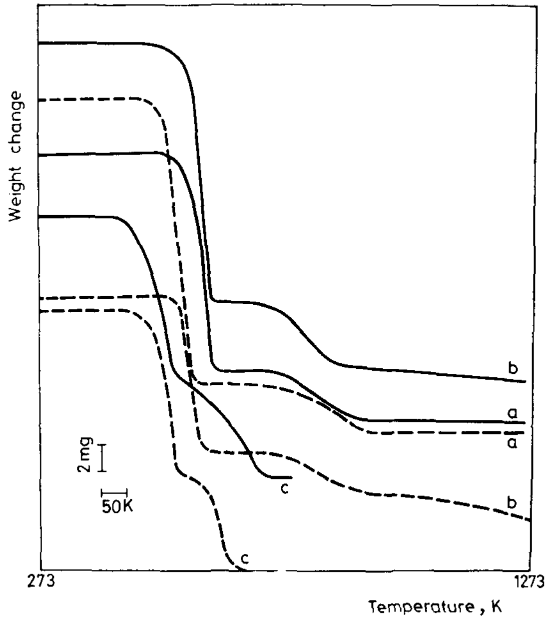


Fig. 1. TG curves of (a) $Zn(S_2CNRR')_2$, (b) $Cd(S_2CNRR')_2$, and (c) $Hg(S_2CNRR')_2$ in N_2 (----) and O_2 (— —) atmospheres

Table 2

Temperature ranges of thermal decomposition and modes of various decomposition reactions

Complex	Decomposition ranges, K	Decomposition reactions	Sample mass, mg	Mass change, mg	
				Expected	Found
$Zn(S_2CNRR')_2$ in N_2	543–643	$Zn(S_2CNRR')_2 \rightarrow Zn(SCN)_2$	38	23.80	23.0
	713–943	$Zn(SCN)_2 \rightarrow ZnS$		6.95	4.0
$Cd(S_2CNRR')_2$ in N_2	548–613	$Cd(S_2CNRR')_2 \rightarrow Cd(SCN)_2$	22	12.56	12.5
	718–943	$Cd(SCN)_2 \rightarrow CdS$		3.49	3.5
$Hg(S_2CNRR')_2$ in N_2	453–553	$Hg(S_2CNRR')_2 \rightarrow HgS$	21	13.13	13.0
	573–728	Volatilization		—	—
$Zn(S_2CNRR')_2$ in O_2	543–633	$Zn(S_2CNRR')_2 \rightarrow ZnS$	26	20.78	17.5
	728–923	$ZnS \rightarrow ZnO$		1.40	4.0
$Cd(S_2CNRR')_2$ in O_2	523–628	$Cd(S_2CNRR')_2 \rightarrow CdS$	35	25.50	21.0
	728–883	$CdS \rightarrow CdO$		1.55	5.0
$Hg(S_2CNRR')_2$ in O_2	443–543	$Hg(S_2CNRR')_2 = HgS$	21	13.13	13.0
	543–728	Volatilization		—	—

ably a volatilization step. Further, zinc and cadmium thiocyanates in nitrogen atmosphere decomposed to yield their respective sulphides at the end of the second step. In oxygen atmosphere, $Zn(S_2CNRR')_2$ and $Cd(S_2CNRR')_2$ decomposed to form their respective sulphides at the end of the first step, while the second step in both cases corresponded to the formation of their respective oxides. Beyond the second step the TG curves were strictly horizontal in both atmospheres in the case of the zinc complex, but as irregular weight loss was observed in the case of the cadmium complex, which provided evidence for the volatile nature of cadmium sulphide and cadmium oxide in nitrogen and oxygen atmospheres, respectively, at higher temperatures. The intermediates and end-products were confirmed qualitatively [15] and quantitatively [13]. Repeated studies of the complexes in oxygen atmosphere revealed that the misleading higher weight of the intermediates was due to incomplete burning of the organic part of the ligand, as evidenced by the quantitative estimation of carbon in the black residue in the intermediate steps. The residues from the Zn(II) and Cd(II) complexes at the end of their first decomposition step in oxygen were found to contain 10.5% and 11.7% of carbon, respectively, which later burned during the second step. Care was taken to detect the presence of sulphate in the residue by the $BaCl_2$ method, but the negative result indicated that the discrepancy in the weight of the residues cannot be attributed to the presence of sulphate in any step involved. The decomposition ranges and corresponding solid-state reactions associated with the above-mentioned studies are given in Table 2.

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References

1. G. D. Thorn and R. A. Ludwig, The Dithiocarbamates and related compounds, Elsevier, New York (1962).
2. D. Coucouvanis, Prog. Inorg. Chem., 11 (1970) 233.
3. R. Eisenberg Prog. Inorg. Chem., 12 (1970) 295.
4. J. Willemse, J. A. Cras, J. J. Steggarda and C. P. Keijers, Structure and Bonding, Springer Verlag, Berlin, Vol. XXVIII (1976) 83.
5. L. H. Pignolet, Topics in Current Chemistry, 56 (1975) 91.
6. A. Hulanicki, Talanta, 14 (1957) 1371.
7. G. S. Whitby and G. L. Matheson, Trans. Roy. Soc. Can., 18, Sect. III (1924) 111.
8. M. A. Bernard and M. M. Bord, Bull. Soc. Chim., France (1969) 3066.
9. G. D. Ascenzo and W. W. Wendlandt, J. Thermal Anal., 1 (1969) 423.
10. S. V. Larionov and L. A. Kosareva, Thermal Analysis, Proceedings Fouth ICTA, Budapest, 1 (1974).
11. H. Gilman and A. H. Blatt, Org. Synth., Collective Vol. I, John Wiley, New York (1958) 448.
12. M. L. Shankaranarayana and C. C. Patel, Anal. Chem., 33 (1961) 1398.
13. A. I. Vogel, A Textbook of Quantitative Inorganic Analysis, Longman Green and Co. Ltd. (1964) 443, 444, 486.
14. J. Chatt, L. A. Duncanson and L. M. Venanzi, Nature, 177 (1956) 1042.
15. A. I. Vogel, A Textbook of Macro and Semimicro Qualitative Inorganic Analysis Orient Longmans Ltd. (1969) 346, 335, 377.

Résumé — On a réalisé la synthèse des complexes des dithiocarbamates bis-*N*-(éthyl, *m*-tolyl) de zinc(II), cadmium(II) et mercure(II), représentés par les formules abrégées $Zn(S_2CNRR')_2$, $Cd(S_2CNRR')_2$ et $Hg(S_2CNRR')_2$, où R et R′ sont respectivement les groupes éthyl et tolyl. Ces complexes ont été caractérisés par analyse élémentaire, détermination de la masse molaire, mesures de conductivité et spectrométrie infrarouge. Les études thermogravimétriques de ces complexes ont été effectuées en atmosphères d'azote et d'oxygène, afin de déterminer leurs modes de décomposition.

Zusammenfassung — Bis-*N*-(äthyl, *m*-tolyl)-dithiocarbamatkomplexe von Zink(II), Cadmium(II) und Quecksilber(II), abgekürzt als $Zn(S_2CNRR')_2$, $Cd(S_2CNRR')_2$ und $Hg(S_2CNRR')_2$, mit R = Äthyl- und R′ = *m*-Tolyl-Gruppe bedeutet, wurden synthetisiert. Diese Komplexe wurden durch Elementaranalysen, Molekulargewichtsbestimmungen, Leitfähigkeitsmessungen und Infrarot-Untersuchungen charakterisiert. Thermogravimetrische Studien dieser Komplexe wurden in Stickstoff- und Sauerstoffatmosphäre durchgeführt um ihre Zersetzungsweise zu bestimmen.

Резюме — Синтезированы бис-*N*-(этил, *m*-толил) дитиокарбамат комплексы цинка(II), кадмия(II) и ртути(II), обозначенные как $Zn(S_2CNRR')_2$, $Cd(S_2CNRR')_2$ и $Hg(S_2CNRR')_2$, R — этил, а R′ — толил. Комплексы охарактеризованы элементарным анализом, определением молекулярного веса, измерением проводимости и инфракрасными спектрами. С целью определения типа разложения этих комплексов, проведены термогравиметрические исследования их в атмосфере кислорода и азота.