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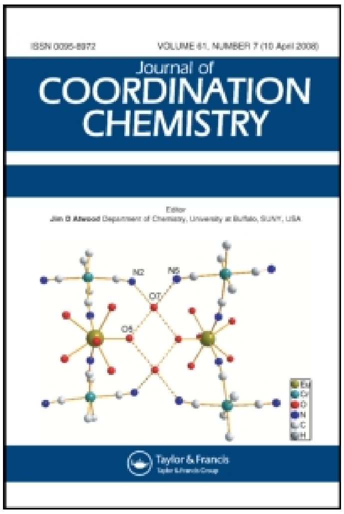

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Enrique Iñiguez[ab]; Jesús Pastor-Medrano[a]; Fernando Ureña-Núñez[c]; Jaime Flores-Estrada[a]; Telésforo J. Morales-Juárez[a]
[a] Facultad de Química de la UAEM, Departamento de Química Inorgánica, CP 50140, México [b] Laboratorio de Química de Plasmas y Estudios Planetarios, Instituto de Ciencias Nucleares, México, DF CP 04510 [c] Departamento de Física, Instituto Nacional de Investigaciones Nucleares, La Marquesa Edo de México, CP 52750, México

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Synthesis and thermal properties of IIB group derived ε-caprolactam-3-dithiocarboxylic acid complexes

ENRIQUE IÑIGUEZ†§, JESÚS PASTOR-MEDRANO†,
FERNANDO UREÑA-NÚÑEZ*‡, JAIME FLORES-ESTRADA† and
TELÉSFORO J. MORALES-JUÁREZ†

†Facultad de Química de la UAEM, Departamento de Química Inorgánica,
Paseo Tollocan S/N, Toluca México, CP 50140, México
‡Departamento de Física, Instituto Nacional de Investigaciones Nucleares,
carretera México-Toluca, La Marquesa Edo de México, CP 52750, México
§Laboratorio de Química de Plasmas y Estudios Planetarios, Instituto de Ciencias Nucleares,
UNAM, Circuito Exterior S/N Ciudad Universitaria, México, DF CP 04510

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Zn(II), Cd(II) and Hg(II) ε-caprolactam-3-dithiocarboxylic acid complexes were synthesized by reacting the ε-caprolactam-3-carbothioic sodium salt with the respective metal salt. Samples were characterized by X-ray powder diffraction, EDS elemental analysis, UV-visible, FT-IR, ^{1}H NMR and EPR spectroscopy. Thermal properties were determined using thermogravimetry and differential scanning calorimetric analysis. M-ε-caprolactam-3-dithiocarboxylic acid complexes showed intense electronic delocalization due to the charge transfer (420 nm) induced from the metal to the dithiolate group reaching different stages into the V unit (350 nm) of the dithiocarboxylate ring with a "$n \rightarrow \pi$" (310 nm) transition. This transition was also observed by EPR which showed 3 parallel and 3 perpendicular signals. The complexes are stabilized by the electro-attraction of the amidic and carbonyl groups; the stability trend is Zn > Cd > Hg. Thermal decomposition shows a multi-step fragmentation process that suggests lactamic chain rupture.

Keywords: Dithiocarboxylates complexes; DSC; TGA; EPR, V-unit

1. Introduction

The dithioacid compounds have been extensively studied, generating numerous patents. Interest in these compounds is due to their chemical and physical properties as well as the development of new applications such as superconductors and photosensitive sensors with polymeric structures. There are few reports on aliphatic derivates of dithioacids, in spite of interesting electrical and magnetic properties similar to carbamates, xanthates and dithiophosphates [1–6]. For soft metal centers such as the IIB group the electronic configuration ($d^{10}s^2$) provides unusual bonding properties,

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*Corresponding author. Email: iniguez@nucleares.unam.mx

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among them a tendency to form stable complexes with tetrahedral or octahedral geometry and low coordination number ca 2 [7]. In this work we report the synthesis, chemical characterization and thermal properties of IIB group ε-caprolactam-3-dithiocarboxylic acid complexes. Additionally we discuss the stability provided by the lactamic ring which prevents easy oxidation of the dithiocarboxylate complexes.

2. Experimental section

2.1. *Materials*

All chemicals used in this work were reagent grade. ε-Caprolactam was obtained from Aldrich Chemical Company and used without further purification. Anhydrous zinc, cadmium and mercury chlorides were dehydrated at 110–120°C for 48 h in a vacuum oven.

2.2. *Preparation of the ligand*

The ligand ε-caprolactam-3-carbothioic sodium salt [Na(DtCapr)] was obtained and purified by following a reported procedure [8] from the reaction of the ε-caprolactam and sodium hydride in tetrahydrofuran. A yellow-red solid was obtained with a yield of 64%.

2.3. *Synthesis of the complexes*

2.3.1. Synthesis of the ε-caprolactam-3-carbodithio-zinc(II) [Zn(DtCapr)]. A solution of zinc chloride (1.36 g, 0.01 mol) in 10 mL of methanol was added dropwise to a stirred methanol solution (20 cm^3) containing ε-caprolactam-3-carbodithioic sodium salt (2.26 g, 0.011 mol) in a water bath. The mixture was stirred at room temperature for one hour. The yellow solid precipitated was washed with cold anhydrous methanol and dried in a vacuum oven at 80°C.

The complexes [Cd(DtCapr)] and [Hg(DtCapr)] were obtained by the same method as for preparation of ε-caprolactam-3-carbodithio-zinc.

All complexes are insoluble in common organic solvents such as ethanol, methanol, acetone, chloroform, benzene and carbon tetrachloride. This insolubility indicates their polymeric nature; however the complexes are fairly soluble in DMSO which allows us to carry out their electronic and ^{1}H-NMR analyses.

2.4. *Spectroscopic and thermal measurements*

Infrared spectra were obtained as KBr pellets (4000–600 cm^{-1}) on a Nicolet FT-SX recording spectrophotometer, frequency calibrated with polystyrene. Ultraviolet and visible spectra were recorded on a Shimadzu UV-160A spectrophotometer in DMSO at concentrations of 10^{-6} M. The EPR spectra were obtained by using a Varian E-15, spectrometer operated at the X-band with 100 kHz modulation of the magnetic field.

Diphenylpicrylhydrazyl (DPPH) ($g = 2.0036$) was used as a field reference. The powder X-ray patterns were obtained at room temperature by using a Siemens D-5000 diffractometer, operated at 40 kV and 30 mA at 1.5435 Å wavelength (Cu-Kα radiation) and nickel filter. Nuclear magnetic resonance spectra were obtained in DMSO-d_6 on a Varian VXR-300 spectrometer with δ measured relative to internal tetramethylsilane (TMS). Elemental microanalyses were obtained by X-ray energy dispersive analysis EDS using an EDAX sounding coupled to a LV Jeol 5900 electronic microscope. All measurements were performed at room temperature. Thermogravimetric analyses were obtained on a TGA-51 (TA instruments) with a 10°C min^{-1} heating ramp under nitrogen atmosphere, using a 5–10 mg sample size per run. Differential scanning calorimetric spectra were recorded on a Perkin-Elmer DSC7, at a 10°C min^{-1} scanning rate under nitrogen.

3. Results and discussion

The reaction between the sodium salt of ε-caprolactam-3-carbodithioic and zinc, cadmium or mercury chlorides leads to the formation of the IIB group derived ε-caprolactam-3-dithiocarboxilic acid complexes as shown in figure 1. The zinc complex was obtained as an amorphous yellow solid with a yield of 79.2%, the cadmium complex is a yellow-orange solid obtained in a yield of 79.9% whilst the yield of the mercury complex obtained as an orange solid was 89.2%. All the complexes are air-stable solids which are insoluble in common organic solvents such as ethanol, methanol, acetone, chloroform, benzene and carbon tetrachloride.

EDS results of elemental composition of the complexes are presented in table 1. In general the experimental analyses are consistent with their theoretical composition ($\alpha < 2$).

3.1. *FTIR and ^{1}H-NMR spectra*

FTIR spectra of the complexes show characteristic absorption bands; however, with the exception of the N–H stretching vibration at 3272.5–3292.3 cm^{-1}, the other molecular vibrations from the precursor were shifted to lower frequencies, e.g., carbonyl group C=O shifts at 1595–1616 cm^{-1}, dithiocarbonyl group C=S at 1098–1024 cm^{-1} and C–S bond at 609–615 cm^{-1}. The shifts result from diverse resonance structures between dithiocarbolate and the lactamic carbonyl. Additionally, an intense signal at 950–1050 cm^{-1} is due to the presence of mercury in the complex, from the symmetric

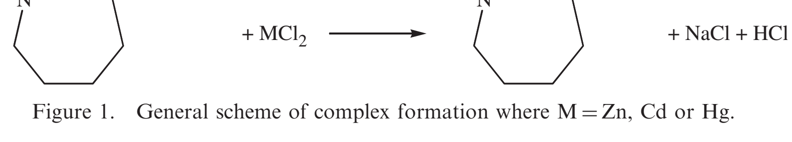


Figure 1. General scheme of complex formation where M = Zn, Cd or Hg.

Table 1. Analytical data of the M^{II+}(DtCapr) complexes.

Complexes	Mw	% Found (Calculated)			
		C	O	S	M
Na(DtCapr)	–	–	–	–	–
Zn(DtCapr)	250.63	36.64	6.15	26.87	28.65
$C_7H_9ONS_2Zn$		(36.62)	(6.96)	(27.93)	(28.47)
Cd(DtCapr)	297.66	30.02	5.95	20.82	40.51
$C_7H_9ONS_2Cd$		(30.39)	(5.78)	(23.18)	(40.63)
Hg(DtCapr)	385.85	22.91	4.28	17.33	54.70
$C_7H_9ONS_2Hg$		(23.04)	(4.38)	(17.57)	(54.98)

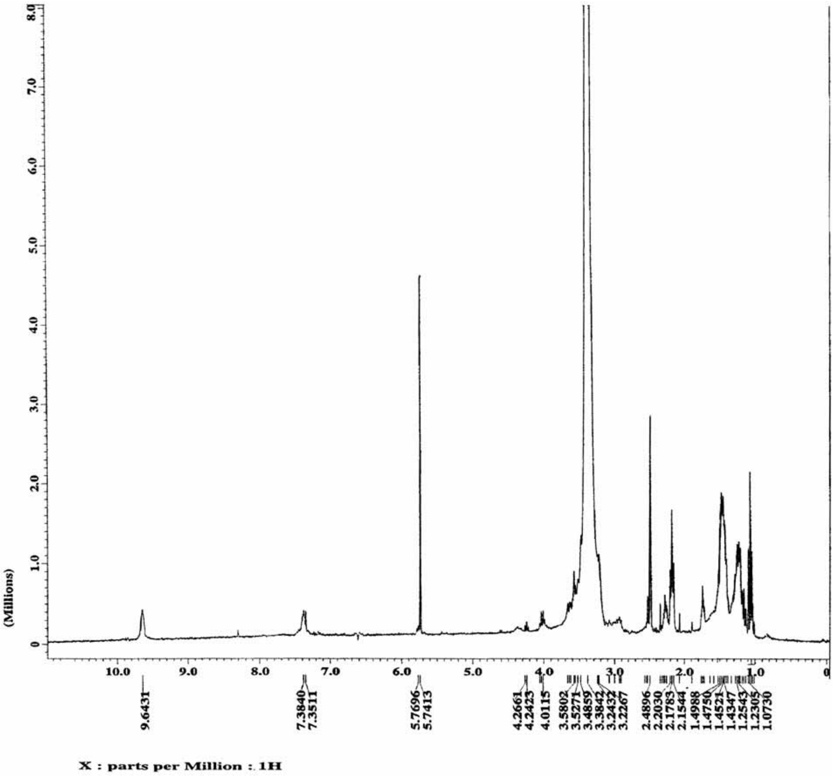


Figure 2. ^{1}H-NMR spectrum of Cd(DtCapr) in DMSO-d_6.

V(C–S) of bidentate coordination mode in dithiocarboxylates according to Ugo Bonatti's criteria [9].

^{1}H-NMR spectra of Cd(DtCapr) and Na(DtCapr) showed sharp and well resolved signals in the lactamic region of the complex. As shown in figure 2 signals from the C_4 hydrogen atoms are displaced to low fields and occur at 2.15–2.20 (1.94–2.36) ppm. The resonance signals centered at around δ 1.38 (1.36) and δ 1.52 (1.55) ppm correspond to the C_5 and C_6 protons, respectively. The C_7 signals are shifted downfield to 3.48–3.58 (3.25) ppm, due to the strong interaction with the more activated nitrogen

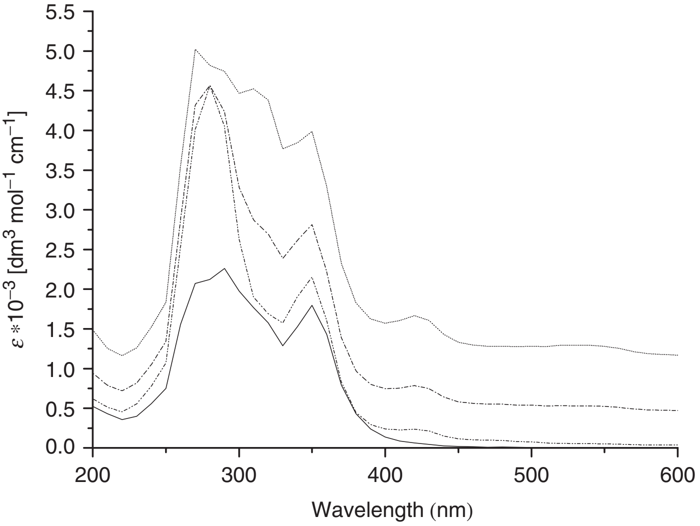


Figure 3. Electronic absorption spectra obtained in 10^{-6} M DMSO. Na(DtCapr) —, Zn(DtCapr) - - -, Cd(DtCapr) ·-·-·- and Hg(DtCapr) · · · ·.

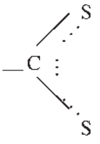
Table 2. Electronic spectral bands of M^{II+}(DtCapr) complexes.

Complexes	λ_{Max} nm (ε, $dm^3\,cm^{-1}\,mol^{-1}$) in DMSO
Na(DtCapr)	270 (2070), 290 (2250), 310 (1760), 350 (1760), 420 (60)
Zn(DtCapr)	270 (4010), 280 (4560), 310 (1890), 350 (2150), 420 (230)
Cd(DtCapr)	270 (4310), 280 (4560), 310 (2870), 350 (2810), 420 (780)
Hg(DtCapr)	270 (5020), 290 (2740), 310 (4520), 350 (3980), 420 (1600)

7.38 (5.60) ppm. It should be pointed out that no signals were found, as expected, for the C_3 protons due to the C=C of the V unit. The Zn and Hg complexes showed a substantial degree of dissociation in DMSO.

3.2. *Electronic and EPR spectra*

Figure 3 illustrates the electronic absorption spectra of the ligand ε-caprolactam-3-carbothioic and metal complexes. The different electronic transitions correspond to dithiocarboxylic group activation as a result of charge transfer between M(II) → S (420 nm), a retro-donation "$n \rightarrow$ V" transition (350 nm), where the V unit is represented by the conjugate group, and a "$n \rightarrow \pi$" transition (310 nm) with activation of resonance in the lactamic ring (290 nm) [10]. The trend in the complex electronic behavior is



related to coupling of both sulfur atoms with the metal ion. Zinc and cadmium complexes show asymmetry between S-M bonds, where distances are concordant with IR asymmetric bands, whereas in the mercury complex both sulfur bonds are equivalent, having intense "$n \rightarrow \pi$" charge transfer transitions due to the higher coordination symmetry seen in other dithiolate complexes [9]. The electronic spectral bands of the M^{2+} (DtCapr) complexes are shown in table 2.

The electron paramagnetic resonance spectra of the complexes are shown in figure 4. The three complexes give similar EPR line patterns with three parallel and three perpendicular which derived from a triplet-state ($S=1$) transition [11, 12]. This state arises from the pair of electrons ($S = ½$ each) shared between the metal and the sulfur atoms. Zn(DtCapr) and Cd(DtCapr) have the same $g=2.0272$ parameter, while for Hg(DtCapr), g is 2.0233. The slight variation observed for g values are probably due to the better coupling of the sulfur atoms with Hg as stated above. The well-defined EPR patterns indicate formation of the complexes.

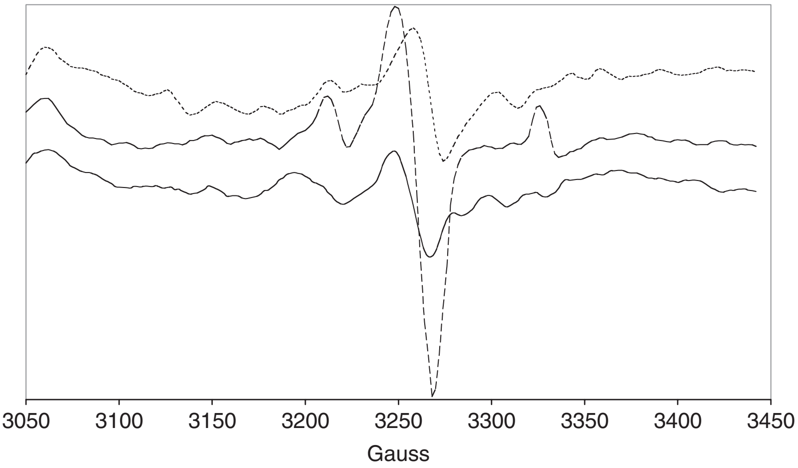


Figure 4. EPR spectra of Zn(DtCapr) —, Cd(DtCapr) - - - and Hg(DtCapr) ·-·-·-.

Table 3. X-ray powder diffraction data of the complex Hg(DtCapr); simple cubic system $a=b=c$.

Powder Patter line	Relative intensities	2θ (Obs.)	2θ (Calcd)	*hkl*
1	29	17.07	16.83	110
2	42	24.25	24.18	011
3	82	29.92	30.09	111
4	80	34.29	35.38	200
5	49	40.21	40.35	020
6	38	46.05	45.18	210
7	36	49.55	50.01	201
8	37	54.49	54.98	021
9	32	59.14	60.3	012
10	–	64.04	66.32	130

3.3. *Powder X-ray diffraction*

The powder X-ray diffraction patterns obtained for M(DtCapr) were almost identical suggesting that the three metal complexes are isostructural. By following Itto's method [13, 14] the powder patterns could be indexed in a simple cubic system. Details of the data collection are summarized in table 3. As the DRX powder patterns of the complexes are comparable we assume that they tend to adopt the preferential tetrahedral coordination geometry noted for this type of complex.

3.4. *Thermal analysis*

Four transitions were determined by DSC analysis (figure 5). The first transition (I) at ~160°C, present in all complexes, corresponds to the opening of the aliphatic chain without loss of mass. Transition II at 183.4–234°C, involves partial aliphatic chain loss; this is only observed for Zn(DtCapr), corresponding to a mass loss of 12.5%. Transitions III and IV, at 302–330°C, are related to an endothermic transition due to chain re-arrangement without a perceptible mass loss in any case. Figure 6 (a, b and c) show the TGA and dTGA analysis of the three complexes. As can be seen, the Zn and Cd complexes suffer gradual fragmentation, ending with the corresponding sulfides, while the mercury complex shows an abrupt loss of mass (60.95%) at 386°C, due to the reduction of the mercury to the element, in agreement with the volatility of elemental mercury. Table 4 summarizes the transitions observed by DSC, the percent weight loss obtained by TGA analysis and the total estimated weight loss fragment for each complex.

In figure 7(a) scheme for thermal fragmentation of the complexes is presented. The entire fragmentation process seems to be proceeded by successive methylene-group loss (160–400°C), while the remaining fragmentation corresponds to the degradation of the aliphatic chain [15, 16]. The residual weight at the end of the decomposition indicates the formation of the corresponding metal sulfides, MS (Zn and Cd) [17].

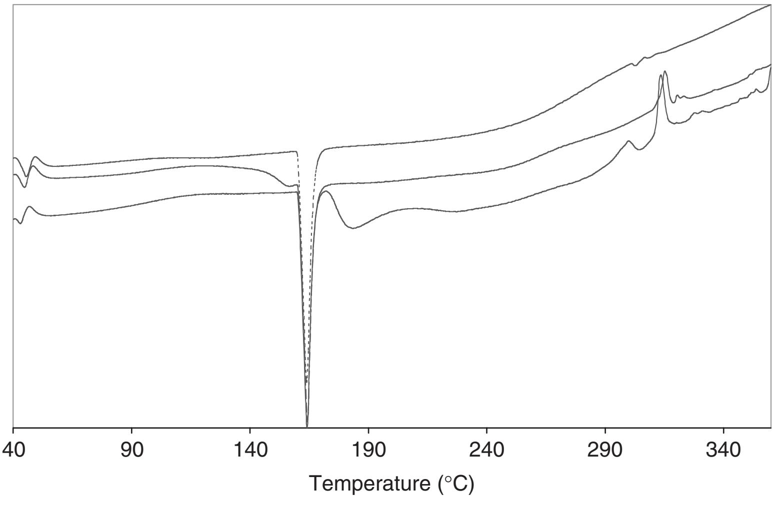


Figure 5. DSC thermal transitions for the Zn(DtCapr), Cd(DtCapr) and Hg(DtCapr) complexes.

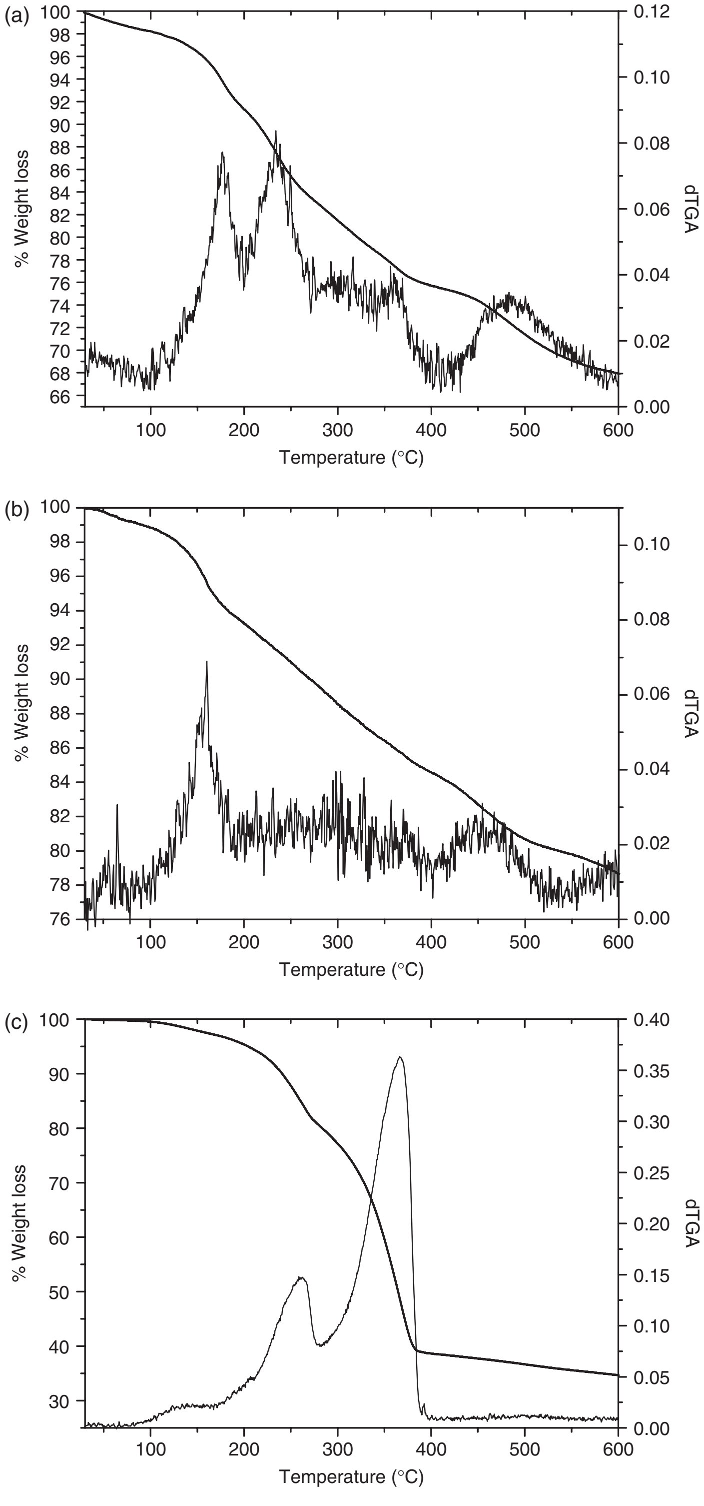


Figure 6. TGA and dTGA spectra of (a) Zn(DtCapr), (b) Cd(DtCapr) and (c) Hg(DtCapr).

Table 4. DSC and TGA data.

	DSC		TGA		
Complex	Transition (°C)	Enthalpy (kcal mol^{-1})	Temp. (°C)	% Total weight loss	Estimated fragment
Zn(DtCapr)	163.91	−2.5	175	5.9	14.96
	183.4	−1.451	234	12.5	16.52
	302.00	0.221	484	27.6	37.67
	313.21	0.736			
Cd(DtCapr)	164.04	−3.103	166	4.9	14.64
	315.20	408.1	447	19.0	42.00
	320.15	399.5			
Hg(DtCapr)	163.77	−3.935	386	60.9	235.21
	301.20				
	306.00				

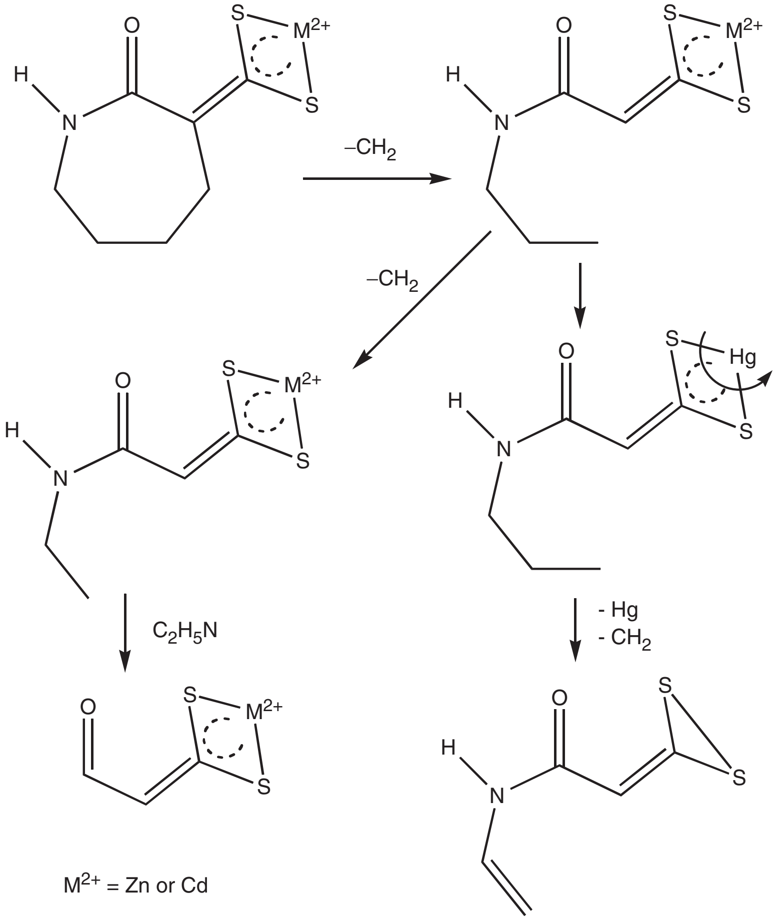


Figure 7. Proposal for the thermal fragmentation of the complexes.

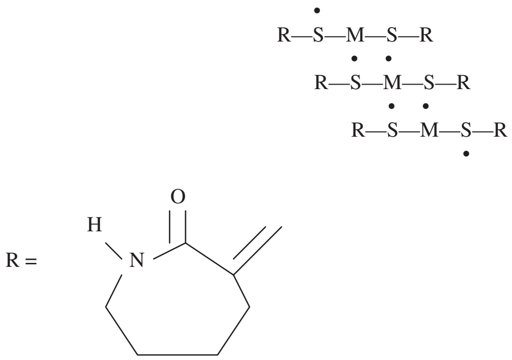


Figure 8. Polymeric structure assumed for the complexes.

Borderline and soft metal centers such as zinc, cadmium and mercury have high affinities for sulphur atoms DtCapr^{2-} forming metal-sulphur bonds. Although the resonance stabilization provided by the lactam group is strong enough to prevent dithioacid oxidation, the thermal stability depends more on the coordination strength of the dithiocarboxylic group with the metal than it does on resonance stabilization.

According to XRD analysis, and consistent with FTIR, UV-Vis, EPR and ^{1}H-NMR spectroscopy results, a bidentate structure for (DtCapr)$^{2-}$ and a polymeric structure for the complexes M (DtCapr) may be assumed as reported by other authors [18, 19], see figure 8.

Acknowledgements

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References

[1] R.D. McLachlan, R.A. Nyquist. *Spectrochim. Acta*, **20**, 1397 (1964).
[2] W.O. Foye. *J. Chem. Edu.*, **46**, 841 (1969).
[3] B.G. Jeliazkova, A. Dimitrova. *Spectrochim. Acta Part A*, **58**, 1163 (2002).
[4] B. Kang, Z. Chen. *Polyhedron*, **17**, 2497 (1998).
[5] S. Niyogi, S. Maiti. *European Poly. J.*, **37**, 2079 (2001).
[6] J.J. Vittal. *Inorg. Chim. Acta*, **343**, 224 (2003).
[7] N. Singh, S. Gupta. *Polyhedron*, **18**, 1265 (1999).
[8] M.J. Janssen. *J. Inorg. Chem.*, **7**, 746 (1972).
[9] S.K. Madan, H.H. Denk. *J. Inorg. Nucl. Chem.*, **27**, 1049 (1965).
[10] D. Coucouvanis, J. Fackler. *J. Amer. Chem. Soc.*, **89**(6), 1346 (1967).
[11] A. Abragam, B. Bleaney. *Electron Paramagnetic Resonance of Transition Ions*, Clarendon Press, Oxford (1970).
[12] W.E. Estes, J.R. Wasson, J.W. Hall, W.E. Hatfield. *Inorg. Chem.*, **17**, 3657 (1978).
[13] R.D. Bereman, D. Nalewajek. *Inorg. Chem.*, **16**, 2687 (1977).
[14] A. Ohno, S. Oae. *J. Organomet. Chem.*, **345**, 237 (1964).

[15] A.C. Draye, O. Persenaire. *Polymer*, **42**, 8325 (2001).
[16] H. Bockhorn, A. Hornung. *Thermochim. Acta*, **337**, 97 (1999).
[17] A. Müller, E. Diemann. *Comprehen. Coord. Chem.*, **2**, 16515 (1987).
[18] H. Krebs, E.F. Weber, H. Fassbender. *Z. Anorg. Allgem. Chem*, **273**, 128 (1954).
[19] K. Bei-Sheng, Ch. Zhong-Ning, S. Cheng-Yong, L. Zhang, W. Ting-Bin. *Polyhedron*, **17**, 15 (1998).