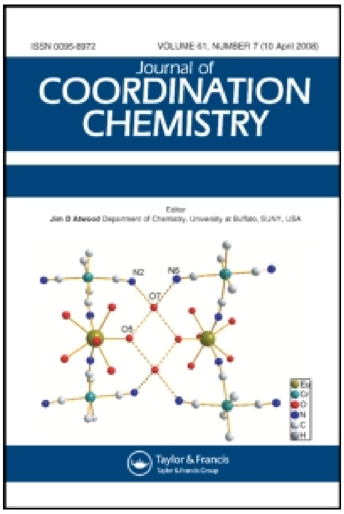

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Synthesis of IIB group derived of N-methyl caprolactam-3-dithiocarboxylic acid complexes: thermal properties

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The synthesis of N-methylcaprolactam-3-dithiocarboxylic acid complexes with the non transition metals Zn(II), Cd(II) and Hg(II) were carried out and the complexes characterized using FT–IR, Raman, XRD, SEM, EDS and elemental analyses. The IR results confirm the link between the caprolactam and the dithiocarboxylate through the C–S bond, whereas Raman spectroscopy gave information about the S–M stretch for each complex. X-ray diffraction analysis shows that the complexes adopt tetrahedral coordination geometry. The SEM showed the morphology of the complexes and the EDS gave a semi-quantitative analysis of the complexes. A comparative study was made among the complexes observing their thermal stability using TGA and DSC. Thermogravimetric study (TGA) indicated different stability of the complexes with the zinc(II) complex most stable.

Keywords: Dithiocarboxylic acids; Caprolactam; Complexes; Transition and non transition metals

1. Introduction

Caprolactams have a resonance hybrid of their primary structure (scheme 1), where oxygen or nitrogen could be donors. The amides have been tested with ions of both transition and non transition metals [1], however there are no systematic studies of their characteristics as electron donors.

Dithioligands have been subject of investigations by Coucouvanis, Fetchin, Bharadwaj and Furlani [2–5], where dithiocarboxylates R–CSS– (R = alkyl, aryl) have been investigated as ligands with transitional and nontransitional metals.

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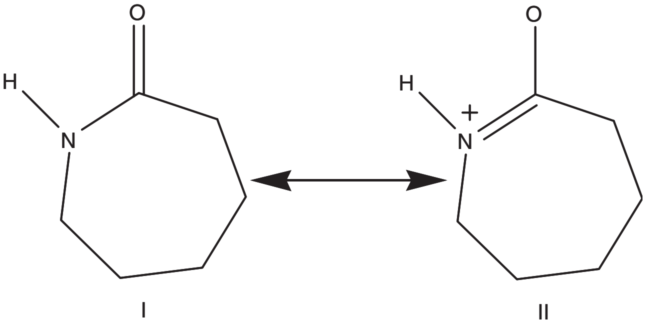
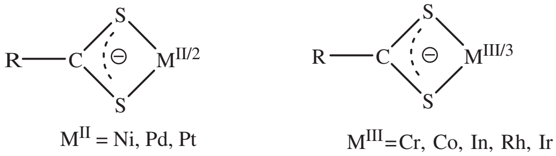


Scheme 1. Resonant structures of α-caprolactam.



R = alkyl or aryl

Scheme 2. Dithiocarboxylates four-member chelate rings.

The dithiocarboxylates are described as bidentate chelates like other dithio anions such as dithiocarbamates, xanthates and dithiophosphates [2–5]. The well-known fourfold coordination in $M^{II}L_2$ and sixfold coordination in $M^{III}L_3$ imply that dithiocarboxylates form four-member chelate rings, as shown in scheme 2 [5].

In this study we obtain N-methylcaprolactam-3-carbodithioate, which was coordinated with Zn(II), Cd(II) and Hg(II) to determine their thermal properties.

2. Experimental

All chemicals used in this research were reagent grade. N-methylcaprolactam was obtained from Aldrich Chemical Company and used without further purification. The metal salts were also obtained from Aldrich Chemical Company without further purification.

2.1. *Preparation of the ligand*

N-methylcaprolactam-3-carbothioic sodium salt was obtained and purified using the reported procedure [6, 7] from the reaction of the N-methylcaprolactam with sodium hydride in anhydrous tetrahydrofuran. The sodium N-methylcaprolactam-3-carbodithioate salt was obtained as an orange-red oil with a yield of 60%. IR-FT (KBr), cm^{-1}: 2928, 2856, 1626, 1495, 1399, 1202, 1079, 863, 559. ^1H NMR (ppm): 3.0, 3.4, 1.6–1.8, 1.85 and 2.2.

2.2. *Synthesis of the complexes*

A solution of metal (Zn^{2+}, Cd^{2+} and Hg^{2+}) chloride (0.01 mol) in 10 mL methanol was added dropwise into a stirred methanol solution (20 mL) containing the corresponding N-methylcaprolactam-3-carbodithioate sodium salt in a water bath. The mixture was stirred at room temperature for one hour and the pH was acidic. The precipitated solid was washed with cold methanol and dried in vacuum [7]. The complexes were recrystallized from $CHCl_3$.

2.3. *Spectroscopic and thermal measurements*

Infrared spectra were obtained as KBr pellets (4000–400 cm^{-1}) on a Nicolet FT–IR 510 spectrophotometer. Raman spectra were obtained from 100–4000 cm^{-1} by using a Microraman LabRam HR 800 Jobinyvon, He–Ne laser Raman spectrophotometer. Scanning Electronic Spectroscopy JEOL 5900 LV operated at 20 kV was used to observe the morphology of the complexes. Elemental analyses were obtained by X-ray energy dispersive analysis EDS using an EDAX sounding coupled to the LV Jeol 5900 electronic microscope. 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. All measurements were performed at room temperature.

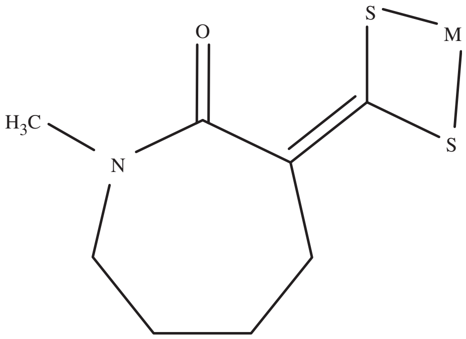
Thermogravimetric analyses were obtained on a TGA-51 (TA Instruments), SDT Q 600. The temperature range was from 25 to 800°C with a 10°C min^{-1} heating ramp under nitrogen using a 5–10 mg sample size per run. Differential scanning calorimetric spectra were recorded on a Perkin–Elmer DSC7 at a 10°C min^{-1} scanning rate under nitrogen from 30 to 390°C using a base line of 20°C.

3. Results and discussion

The general formulas of the complexes formed between sodium N-methylcaprolactam-3-carbodithioic and the zinc(II), cadmium(II) and mercury(II) chlorides is shown in figure 1. N-Methylcaprolactam-3-carbodithio-zinc(II) [Zn(m-dtcc)] was an amorphous pale yellow solid with a yield of 31%; N-methylcaprolactam-3-carbodithio-cadmium(II) [Cd(m-dtcc)] was an amorphous yellow solid with a yield of 45%, and N-methylcaprolactam-3-carbodithio-mercury(II) [Hg(m-dtcc)] was an amorphous grey solid with a yield of 52%, elemental analyses; C: 24.55 (24.59), O: 4.42 (3.58), N: 5.53 (4.09), Hg: 56.45 (51.33). All the complexes are air stable solids insoluble in common organic solvents such as ethanol, methanol, acetone and benzene, sparingly soluble in chloroform, carbon tetrachloride and DMSO at room temperature.

3.1. *FT–IR and Raman spectra*

IR spectra (Supplementary Data) for N-methylcaprolactam complexes [M(m-dtcc)] show methyl and methylene CH_3, CH_2 shifts at 2853–2923 cm^{-1}, the C=O vibration at 1597–1633 cm^{-1}, the N–C=O shift at 1386–1454 cm^{-1}, C=S absorption band at 1011–1159 cm^{-1} and C–S at 589–682 cm^{-1}, table 1 [7–12]. The main feature of Raman spectra was the occurrence of moderately intense peaks around 250, 325 cm^{-1}, which



M=Zn(II), Cd(II),
and Hg(II)

Figure 1. General scheme of the complexes.

Table 1. FT–IR and Raman vibrations of N-methylcaprolactam-3-carbodithio-metal complexes, M(m-dtcc).

Signal[a]	Zn(m-dtcc)	Cd(m-dtcc)	Hg(m-dtcc)	
Spectra	FT-IR	FT-IR	FT-IR	Raman
CH3 CH2	2931	2923	2923	
	2858	2853	2853	
C=O (amide)	1621	1633	1597	
N–C=O	1561	1633	1453	
	1454			
C=S	1128	1159	1115	
	1052	1011	1001	
C–S	682	654	579	
M–S				320
				250

[a] cm^{-1}.

can be assigned to Hg–S vibration from Hg(m-dtcc). The C=S, C–S and M–S were the principal vibrations in the IR and Raman spectra to identify the presence of the complexes. The vibration bands of the compounds showed similar behavior and with sulphur complexes synthesized by Dai *et al.* [10], Burke and Fackler [4], Singh and Gupta [11], Ivanova [12] and Ivanova *et al.* [13].

The Raman spectrum (Supplementary Data) presented the characteristic band for S–M and this vibration suggests that the metal coordinated with the sulphur atoms in a four-member chelate [7, 12, 13].

The four-member ring, two sulphurs, carbon and the metals resulted in shorter and stronger bonds than normal, therefore the C=O; C=S and C–S bands shifted to lower frequencies.

3.2. *Scanning Electron Microscopy* (*SEM*)

All complexes showed different morphology (Supplementary Data). The Zn(m-dtcc) is cumulus formed from small aggregates. The Cd(m-dtcc) shows irregular aggregates from different sizes and Hg(m-dtcc) forms aggregates like rocks.

3.3. *Powder X-ray diffraction*

The synthesized complexes showed almost identical powder X-ray diffraction patterns, suggesting isostructural complexes. These patterns are indexed in a simple cubic system, table 2, according to those reported by Iñiguez [7], adopting a tetrahedral geometry as expected.

3.4. *Thermogravimetric analyses* (*TGA*)

Figure 2 shows a sample TGA and dTGA of the complexes and their degradation steps are presented in table 3. Thermal analyses by TGA from 20–800°C the Zn and Cd complexes show similar thermal behavior, but the Hg complex showed different thermal behavior.

The first mass loss (16%) for Zn(m-dtcc) (figure 2) occurs between 150–225°C corresponding to loss of part of the aliphatic chain at 181.85°C, the second loss from 225 to 525°C with maximum loss in 492.23°C (12%) completes the aliphatic chain loss. The DSC does not show considerable energy changes between 30–390°C, only visible in an endothermic peak at 375°C, showing decomposition of the complex.

Table 2. X-ray powder diffraction data of Cd(m-dtcc); simple cubic system a = b = c.

Powder pattern line	Relative intensities	2θ (Obs.)	2θ (Calcd)	*hkl*
1	50	16.00	16.83	110
2	60	24.10	24.18	011
3	100	30.15	30.09	111
4	40	33	35.38	200
5	43	37	40.35	020
6	33	48	45.18	210
7	46	50.10	50.01	201
8	32	53.50	54.98	021
9	26	58.55	60.3	012
10	31	63.15	66.32	130

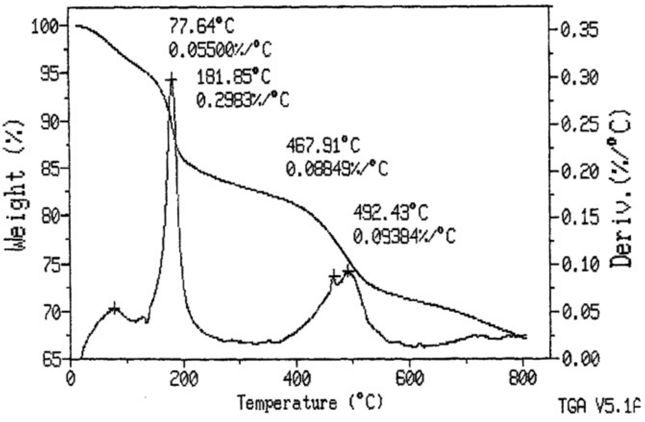


Figure 2. TGA and dTGA spectra of the zinc complex.

Table 3. Fragments of the thermal decomposition of N-methylcaprolactam-3-carbodithioate complexes.

Complex	Temp (°C)	% Total weight loss	Estimated fragment
Zn(m-dtcc)	20	0	0
	181.85	16	42.62
	492.43	12	27.98
Cd(m-dtcc)	20	0	0
	257.45	6	18.88
	335.10	5	14.79
	600.72	19	53.39
	788.70	27	61.46
Hg(m-dtcc)	20	0	0
	254.81	50	201.45
	329.81	39	122.88

The TGA of Cd(m-dtcc) (Supplementary Data) showed four degradations, the first one between 220–300°C (6%) (257.45°C) and the second corresponds to 5% (335.10°C) in the range 300–380°C. From 380° to 650°C loss of 19% (600.72°C) completes loss of the aliphatic chain and a final loss of 27% at 788.70°C. The residual at the end of decomposition corresponds to the metal disulfide [7]; in the DSC only a gradual decomposition was observed starting at 260°C.

In the mercury complex DSC (Supplementary Data) an exothermic peak in the range 225 to 250°C is the first abrupt loss of mass of the complex (49%) according to the TGA at range between 220 to 280°C (maximum loss at 254.81°C) was associated with the loss of the mercury due to reduction of it during the thermal treatment. A second loss was observed from 225–250°C (40%) corresponding with loss of lactam.

The Zn and Cd complex fragmentations begin with gradual loss of the aliphatic chain [14]. The residual weight at the end of the decomposition of the Cd complex suggests that a metal sulphide remains [7, 15, 16]; however in the Zn complex the residual weight percentage is higher, implying that Zn(m-dtcc) has part of the lactam after decomposition. The thermal stability Zn > Cd > Hg depends strongly on the metal ion and is in agreement with metal–ligand strength [17].

4. Conclusion

The complexes are stable at room temperature. The presence of methyl in the lactam gives the complexes major stability when compared with the ε-caprolactam complexes [7], due to the electron density of CH_3. As a consequence the decomposition temperature of N-substitute complexes is higher than the α-caprolactam complexes.

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