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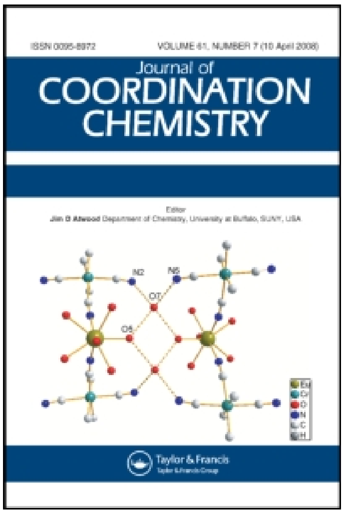

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Synthesis, Characterization and Thermal Behavior of Complexes of Cu(II), Zn(II) and Cd(II) with S,S'-Methylenebis(Cysteine)

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SYNTHESIS, CHARACTERIZATION AND THERMAL BEHAVIOR OF COMPLEXES OF Cu(II), Zn(II) AND Cd(II) WITH S,S′-METHYLENEBIS(CYSTEINE)

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Synthesis and characterization, including data on thermal decomposition, are reported for the complexes of S,S′-methylenebis(cysteine) (djenkolic acid) with copper(II), zinc(II) and cadmium(II): $CuC_7H_{12}N_2O_4S_2$ [I]; $ZnC_7H_{12}N_2O_4S_2$ [II] and $CdC_7H_{12}N_2O_4S_2$ [III]. X-ray diffraction showed that the compounds are isostructural and belong to a monoclinic system. According to IR spectra, COO, NH_2 groups and bridging sulfur atoms are the main coordination sites.

Keywords: S,S′-methylenebis(cysteine); Djenkolic acid; Transition metals; Complexes

INTRODUCTION

It is of common knowledge that some transition metals exert pronounced biological effects, functioning as active centers within important bioactive molecules in living systems. Among such metals are copper, zinc and cadmium, which represent a group of elements with similar coordination tendencies and play a significant role in cell metabolism [1]. The most important zinc proteins are Cu-Zn superoxide dismutases, alcohol dehydrogenase and a variety of hydrolases [2]. Cadmium, because of its high affinity to cellular binding sites, gives rise to the poisonings in alterations of hepatic aminoacids transformation [3] and aminoacid transport in the kidney of animals [4]. Nevertheless, aminoacids of vegetal origin have not been widely tested as potential ligands for complex formation in spite of their nutritional and metabolic importance. S,S′-methylenebis(cysteine) or djenkolic acid, as well as its derivatives, were shown to possess a net antioxidant and rejuvenating activity, due to their capacity

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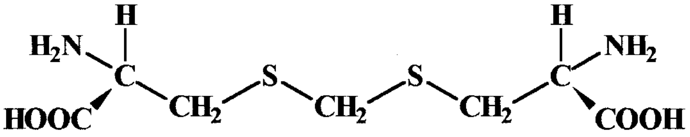

FIGURE 1 Structural formula of S,S′-methylenebis(cysteine).

for reactivation of cell metabolism [5]. Earlier only the complexes with Co(II) and Ni(II) with this ligand have been investigated [6].

The present study deals with synthesis and characterization of novel complexes of copper(II), zinc(II) and cadmium(II) with S,S′-methylenebis(cysteine) taken in the form of the djenkolate anion, as the first step for preparation of virtual chemical modulators and pharmaceutical trappers. Figure 1 shows the structure of S,S′-methylenebis(cysteine).

EXPERIMENTAL

Materials and Methods

S,S′-methylenebis(cysteine); sodium carbonate; zinc(II) sulfate heptahydrate; copper(II) sulfate pentahydrate; cadmium(II) nitrate tetrahydrate and ethyl alcohol were Aldrich and Sigma products, analytical-grade purities.

Elemental analyses of carbon, hydrogen and nitrogen were performed using a CHNS-O EA1110 Analyzer, CE Instruments with high purity cysteine were used as a reference substance. Copper, cadmium and zinc contents were determined by the Atomic Absorption technique using a Perkin Elmer A Analyst 300. X-ray powder diffraction measurements were performed on a Siemens Kristalloflex diffractometer, Cu-Kα radiation, Ni-filter. Lattice parameters were refined using the complex of programs AFPAR based on least-square method. UV–Visible spectra of the complexes (diffusion reflectance) were registered on a fiber optics Spectrophotometer Guide Wave, model 260 in the region 1700–360 nm. Infrared spectra were recorded on a FT-IR Spectrophotometer Spectrum 2000, Perkin Elmer: Samples were prepared in the form of CsI pellets. EPR spectra were recorded under liquid nitrogen by using a Bruker Spectrometer for solid samples. Thermal analysis was performed on a Thermoanalyzer TG/DTA simultaneous SDT 2960 TA Instruments under the following conditions: synthetic air, 100 mL/min, and heating at 20°C per minute, from 30 to 1100°. In parallel, a static assay was performed, which consisted of heating the complexes at the temperatures chosen in accordance with the landings observed on the TG curves.

Preparation and Solubility Determinations

Djenkolic acid is practically insoluble in water, and hence its soluble alkaline salt was used as the reagent containing readily available djenkolate-ion. For the conversion, a fine suspension of 0.5086 g (0.002 mol) of djenkolic acid in water was heated up to 90°C and then 0.2119 g (0.002 mol) of sodium carbonate was added under continuous stirring until the solution turned clear. Copper, zinc and cadmium complexes were precipitated by the reaction of this solution with the solutions of the Cu, Zn and Cd salts also taken in stoichiometric proportions [0.4994 g of $CuSO_4 \cdot 5H_2O$ (0.002 mol); 0.5751 of $ZnSO_4 \cdot 7H_2O$ (0.002 mol) and 0.6169 g of $Cd(NO_3)_2 \cdot 4H_2O$ (0.002 mol)]. Polycrystalline solids precipitated immediately. Crystals were filtered and dried over P_4O_{10} at room temperature. No single crystals could be obtained in order to perform a full X-ray study.

Chemical analysis rendered the following values: Calcd. for $CuC_7H_{12}N_2O_4S_2$(%): C, 26.62; H, 3.83; N, 8.87; Cu, 20.12. Found: C, 25.76; H, 4.23; N, 8.31; Cu, 21.82. Calcd. for $CdC_7H_{12}N_2O_4S_2$(%): C, 22.99; H, 3.58; N, 7.66; Cd, 30.72. Found: C, 22.18; H, 3.29; N, 7.20; Cd, 30.76. Calcd. for $ZnC_7H_{12}N_2O_4S_2$(%): C, 26.29; H, 3.78; N, 8.76; Zn, 20.45. Found: C, 25.92; H, 4.09; N, 8.48; Zn, 20.32. Additional experiments showed that the complexes have the same compositions after being precipitated at different molar ratios Me-L.

The samples left at room conditions may absorb small quantities of water which is easily removed by heating at low temperatures. The compounds exhibit very poor solubility in water, methanol, ethanol, and other organic solvents with no signs of solvolysis. The solubilities in water at 25°C were determined by analyzing the metal contents after stirring together solid and aqueous phase for 3 weeks and longer. Aliquots of 50 mL were periodically analyzed until the equilibrium was achieved. The solubilities are: 7.5×10^{-6} mol L^{-1} for $CuC_7H_{12}N_2O_4S_2$, 4.3×10^{-6} mol L^{-1} for $ZnC_7H_{12}N_2O_4S_2$ and 1.0×10^{-5} mol L^{-1} for $CdC_7H_{12}N_2O_4S_2$.

RESULTS AND DISCUSSION

A full electron diffraction study could not be accomplished owing to instability of the sample under electron beam. However, this method permitted the initial choice of the approximate values of the lattice parameters as 11, 6 and 7 Å. Thus, an orthorhombic system, or even a monoclinic system, with an angle near 90° could have been envisaged as possible. In fact, indexing of the X-ray powder pattern was successfully done on a monoclinic cell for the three complexes. A representative indexation of $CdC_7H_{12}N_2O_4S_2$ by X-ray diffractogram is reported in Table I. Calculated lattice parameters are reported in Table II.

Copper complex EPR spectrum shows isotropic and anisotropic resonance lines in the range 2700–3400 gauss. Four hyperfine lines with $g_{\parallel} = 2.3686$ and $A_{\parallel} = 166.07$ gauss are present. In addition, the anisotropy generates a signal with $g_{\perp} = 2.1499$. This pattern suggests for the copper atom an axial symmetric geometry [7,8], that is, in an octahedral or square planar symmetry.

Cu^{2+} ion has a $\boldsymbol{d}^9$ electronic configuration and originates only one spectral term in electronic spectra, $^2\boldsymbol{D}$. The *d–d* electronic transition in an octahedral field is $t_{2g}^6 e_g^3(^2E_g) \rightarrow t_{2g}^5 e_g^4(^2T_{2g})$, corresponding to 10 Dq. Therefore, a single band in the electronic spectra is expected for the $\boldsymbol{d}^9$ configuration with a possible unfolding of this band because of Jahn-Teller distortion [9]. In fact, electronic spectrum of the copper complex, reported in Fig. 2, presents only one band centered at 16950 cm^{-1}.

Infrared spectra of $CuC_7H_{12}N_2O_4S_2$, $ZnC_7H_{12}N_2O_4S_2$, $CdC_7H_{12}N_2O_4S_2$, djenkolic acid and alkaline salt of djenkolic acid (reference compound) are reported in Fig. 3. It was postulated elsewhere [10] that the difference between the vibrational ν_{as} (COO^-) and ν_{sym} (COO^-) modes, Δ, in aminoacids, generally grows with increasing the M–O bond strength. This difference should be higher for the complexes than for

TABLE I Indexation of X-ray powder diffraction data for $CdC_7H_{12}N_2O_4S_2$

h	*k*	*l*	d_{calc}	d_{obs}	I/I_0
1	0	0	11.59	11.57	80
2	0	0	5.79	5.75	37
1	1	$\bar{1}$	4.73	4.70	37
1	1	1	4.51	4.48	100
2	0	1	4.25	4.26	41
2	1	$\bar{1}$	3.93	3.97	36
3	0	$\bar{1}$	3.50	3.51	11
0	2	$\bar{1}$	3.26	3.30	15
1	2	$\bar{1}$	3.17	3.20	5
1	2	1	3.10	3.11	15
1	1	2	2.95	2.95	9
4	0	$\bar{1}$	2.76	2.74	12
2	1	2	2.66	2.65	12
1	2	$\bar{2}$	2.49	2.49	38
5	0	0	2.32	2.32	5
2	2	2	2.255	2.250	8
4	1	2	2.041	2.044	3
1	3	$\bar{2}$	1.992	1.986	4
3	2	$\bar{3}$	1.792	1.791	2
5	1	$\bar{3}$	1.661	1.660	3
5	2	$\bar{3}$	1.548	1.548	2

TABLE II Calculated lattice parameters for the three complexes*

	Compounds		
Parameters	$CuC_7H_{12}N_2O_4S_2$	$ZnC_7H_{12}N_2O_4S_2$	$CdC_7H_{12}N_2O_4S_2$
a, Å	11.29	11.15	11.63
b, Å	7.40	7.34	7.41
c, Å	6.86	6.85	6.88
β, deg	95.63	94.40	95.04

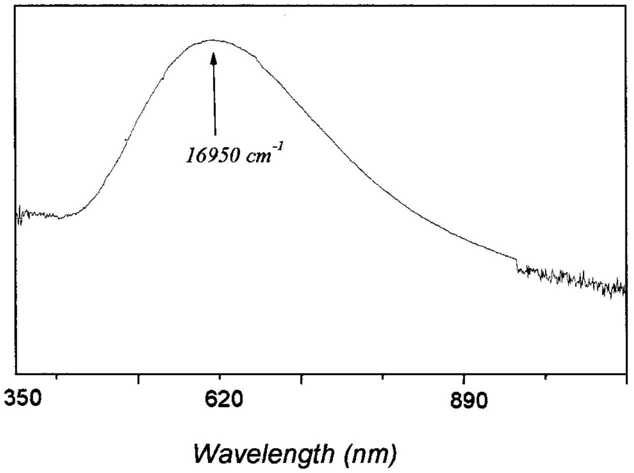

FIGURE 2 Electronic absorption spectrum of $CuC_7H_{12}N_2O_4S_2$.

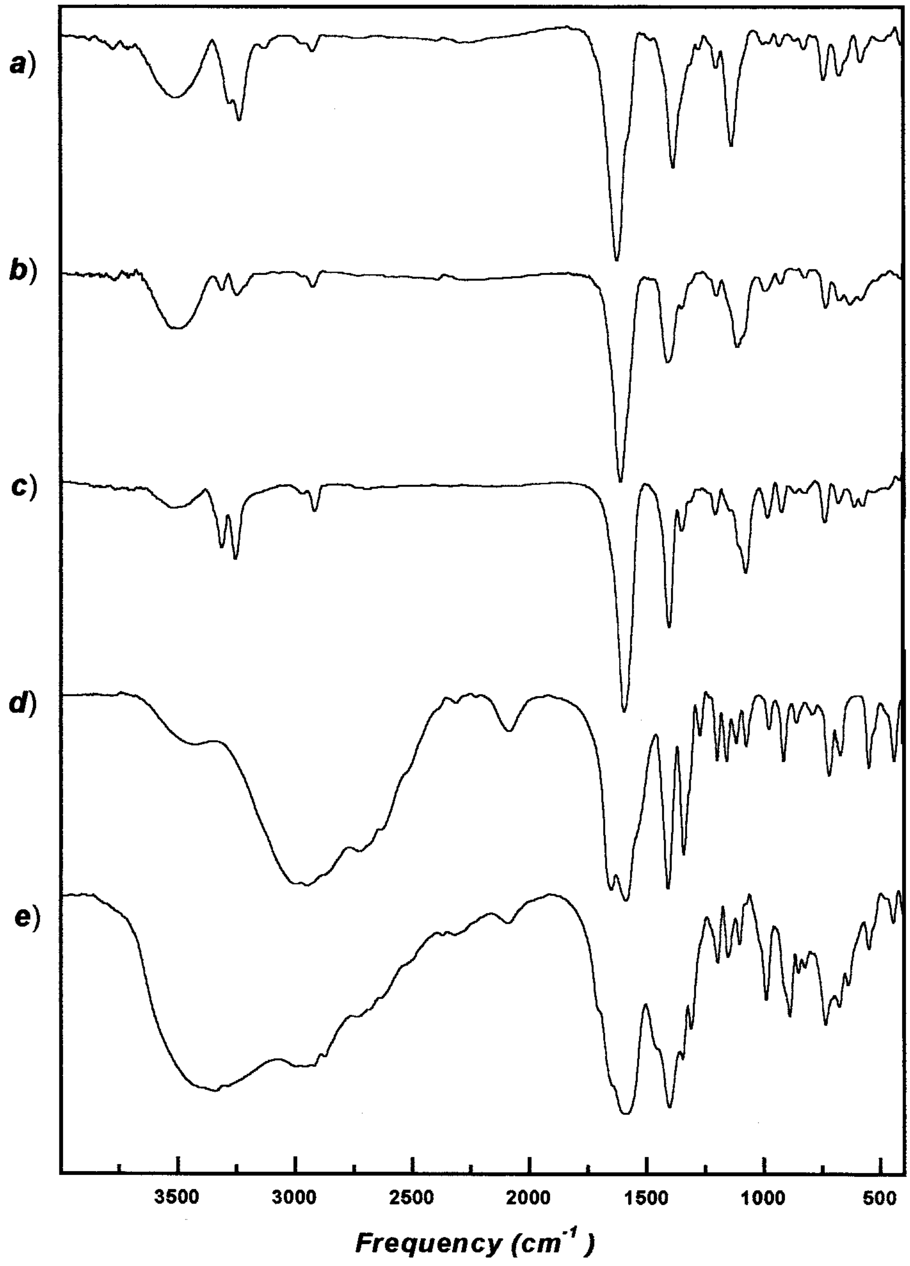

FIGURE 3 Infrared absorption spectra of the compounds: (a) $CuC_7H_{12}N_2O_4S_2$; (b) $ZnC_7H_{12}N_2O_4S_2$; (c) $CdC_7H_{12}N_2O_4S_2$; (d) djenkolic acid; (e) potassium djenkolate.

the djenkolate. In fact, in our case: $\Delta_{\text{postassium-djenkolate}} = 188\,\text{cm}^{-1}$, $\Delta_{\text{Cu-djenkolate}} = 240\,\text{cm}^{-1}$, $\Delta_{\text{Zn-djenkolate}} = 201\,\text{cm}^{-1}$ and $\Delta_{\text{Cd-djenkolate}} = 191\,\text{cm}^{-1}$. Thus, comparison of the IR spectra of the complexes with the data available for djenkolic acid and potassium djenkolate show that the coordination occurs through the carboxylate group.

Two well-resolved bands at 3450 and 3280 cm^{-1}, as a rule, reflect the interactions of the metal cation with the amino group [11]. In the potassium djenkolate spectrum, a broad band in the region 3100–3350 cm^{-1} corresponds to the frequencies of the NH_2 group, while in the spectrum of the djenkolic acid these frequencies are observed in the range 2600–3200 cm^{-1}. The merging and shift of the bands suggest that amino group protons are involved in the formation of hydrogen bonds, which are characteristic for djenkolic acid and its derivatives [12]. For the complexes, a significant amino group involvement is confirmed by the presence of the bands at 3268–3235 cm^{-1} (copper), 3306–3246 cm^{-1} (zinc) and 3309–3251 cm^{-1} (cadmium), typical of the NH_2 stretching vibrations. An additional evidence of such coordination is the fact that the band commonly observable in the range 2050–2100 cm^{-1} does not appear in the spectra of the complexes. This band would be characteristic of a free NH_2 group [13].

The third available coordinating site is the thioether C-S-C bridging group. However, no displacements in C-S vibrational modes were observed when comparing those characteristic for djenkolic acid and the frequencies found for the complexes (672 and 670–674 cm^{-1}, respectively). In this case, additional evidences are needed to confirm the coordination via sulfur. For this purpose a combination of thermal analysis and IR spectroscopy is useful.

Samples of $CdC_7H_{12}N_2O_4S_2$ were heated at the temperatures corresponding to the plateaux in TR curve (Fig. 4). The attributions of diffractograms made on the basis of the X-Ray International System Database [14] permitted in identifying CdS (550°C) and $Cd_3O_2SO_3$ (750°C). A third sample obtained after heating at 1100°C was identified

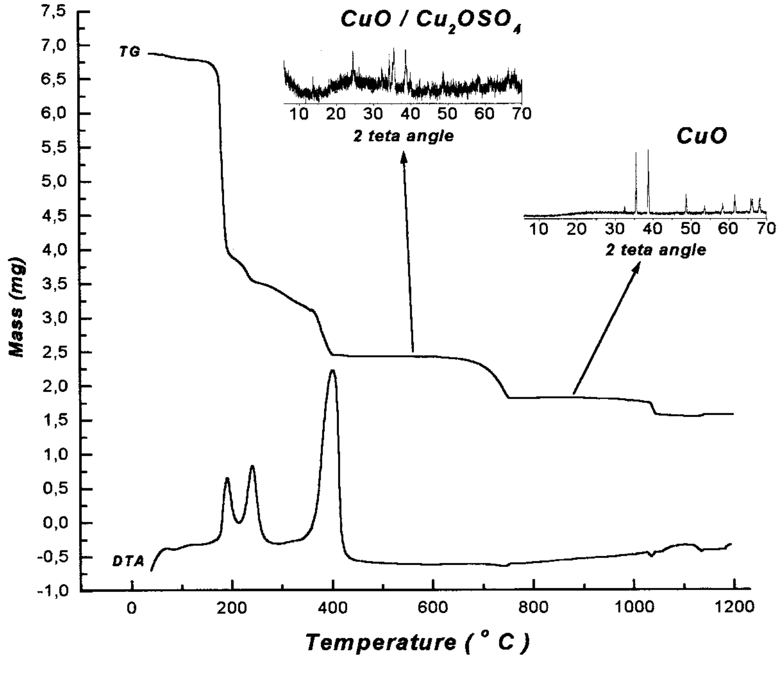

FIGURE 4 TG and DTA curves of $CuC_7H_{12}N_2O_4S_2$ with X-ray diffractograms of the intermediate compounds.

as CdO. Thus, CdS may be considered as an intermediate decomposition product which undergoes oxidation to give $Cd_3O_2SO_3$. The other complex, $ZnC_7H_{12}N_2O_4S_2$, heated until 900°C, showed a behavior similar to the above cadmium compound, e.g., the first step is the formation of ZnS, which is transformed into oxide, ZnO. No oxoderivative intermediates, in this case, could be identified. In the case of the copper complex, $CuC_7H_{12}N_2O_4S_2$, heating at 570°C generates a product identified as a mixture of CuO and Cu_2OSO_4. According to TG curve, Cu_2OSO_3 starts to form around 430°C, undergoes oxidation to Cu_2OSO_4 and is converted into CuO (Figs. 4–6).

Formation of metal sulfides and oxosulfates during thermal decomposition is in itself an indirect indication of the metal-sulfur coordination in the complexes. Nevertheless, more convincing proof was provided by analyzing IR spectral data in the region 250–350 cm^{-1} where metal-sulfur stretching vibrations are usually present. For cadmium djenkolate, in particular, a characteristic frequency Cd-S is given as 247 cm^{-1} [15,16]. The value found in our spectra is surprisingly the same. Moreover, IR spectrum of commercial sulfide also gives 247 cm^{-1}. For zinc djenkolate the metal-sulfur stretching vibrations were described at 276 cm^{-1}. The thermodecomposition residue of the complex, shows the corresponding vibrations at 284 cm^{-1} and the commercial sample gives the same value. IR spectra of the cadmium and zinc complexes and respective metal sulfides are reported in Figs. 7 and 8. As to the copper sulfide, spectra quality does not permit drawing unambiguous conclusions.

These results for sulfur coordination are consistent with the well known affinity of divalent transition elements to thioether groups contained in animal proteins [2].

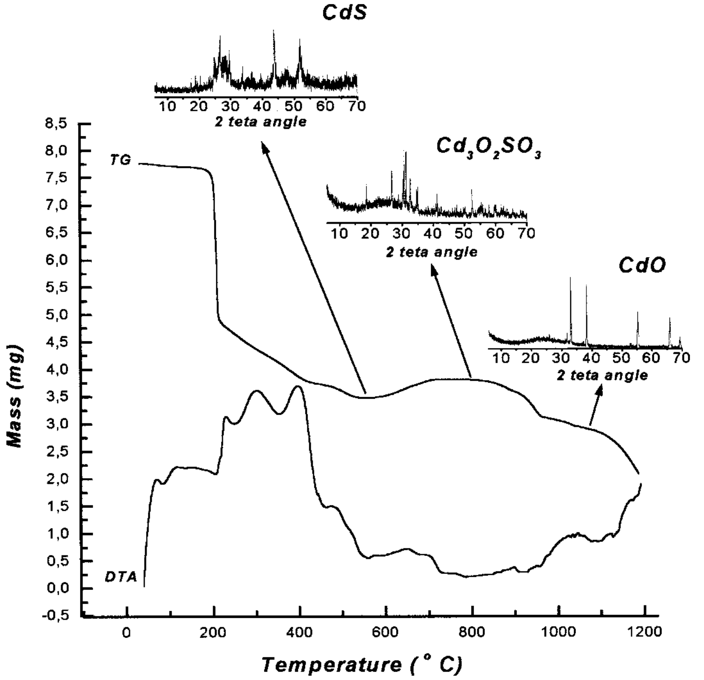

FIGURE 5 TG and DTA curves of $CdC_7H_{12}N_2O_4S_2$ with X-ray diffractograms of the intermediate compounds.

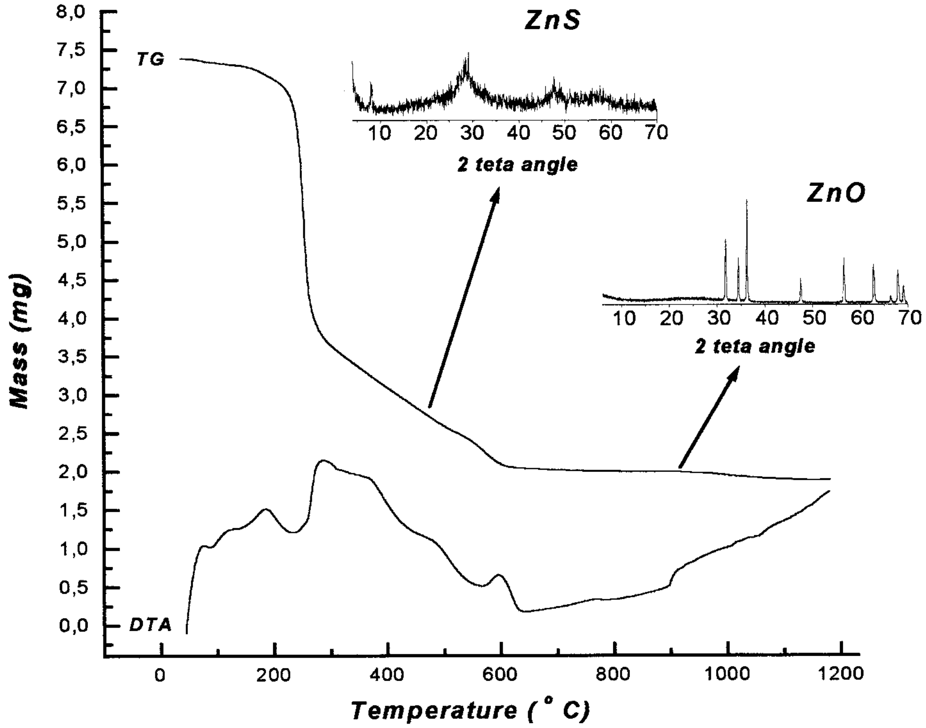

FIGURE 6 TG and DTA curves of $ZnC_7H_{12}N_2O_4S_2$ with X-ray diffractograms of the intermediate compounds.

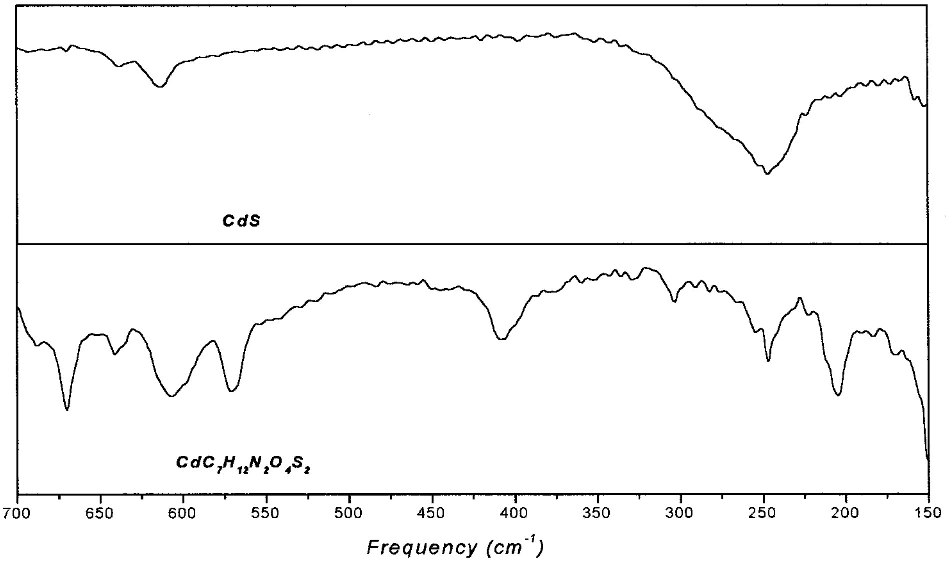

FIGURE 7 Infrared absorption spectra of CdS and $CdC_7H_{12}N_2O_4S_2$.

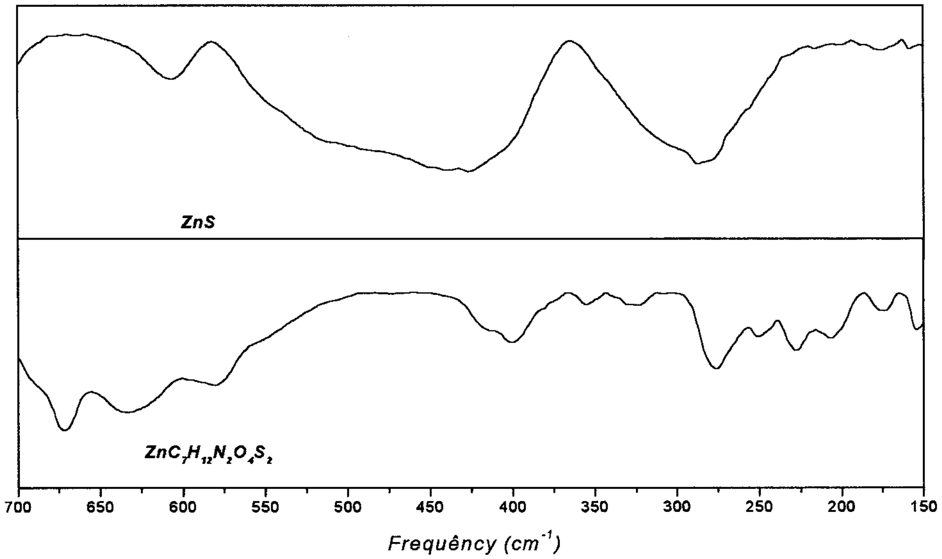

FIGURE 8 Infrared absorption spectra of ZnS and $ZnC_7H_{12}N_2O_4S_2$.

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References

[1] H. Sigel (1979). *Metal Ions in Biological Systems*, Vol. 9, p. 112. Marcel Dekker Inc., New York.
[2] I. Bertini, H.B. Gray, S.J. Lippard and S.J. Valentine (1994). *Bioinorganic Chemistry*, p. 3. University Science Books, California.
[3] F. Yamasaki, M. Kurasaki, S. Oikawa, T. Emoto, M. Ocabe and Y. Fojima (1997). *Cellular and Molecular Life Sciences*, **53**, 459.
[4] E.C. Foulkes and S. Blanck (1992). *FASEB Journal*, **6**, 1855A.
[5] H.U. Weber, J.F. Fleming and J. Miguel (1982). *Arch. Gerontol. Geriatr.*, **1**, 299.
[6] P.P. Corbi, M. Cavicchioli, P. Melnikov, A.C. Massabni and L.A.A. Oliveira (2000). *Rus. J. Coord. Chem.*, **26**, 31.
[7] S.J. Lippard and J.M. Berg (1994). *Principles of Bioinorganic Chemistry*, p. 83. University Science Books, California.
[8] P.F. Knowles, D. Marsh and H.W.E. Rattle (1976). *Magnetic Resonance of Biomolecule*, p. 185. John Wiley & Sons, London.
[9] D.F. Shriver, P.W. Atkins and C.H. Langford (1994). *Inorganic Chemistry*, p. 589. Oxford University Press, Oxford.
[10] K. Nakamoto, Y. Morimoto and A.E. Martell (1961). *J. Am. Chem. Soc.*, **83**, 4528.
[11] J.V. Quagliano, L.M. Vallarino and C.A. McAuliffe (1966). *Inorg. Chem.*, **5**, 1996.
[12] P. Melnikov, A. Cuin, P.P. Corbi, M. Cavicchioli and A.C. Massabni (1998). *Proceedings of the Fifth International Conference on Heteroatom Chemistry*, p. 97. London, Ontario, Canada.
[13] R.M. Silverstein, G.C. Bassler and T.C. Morrill (1991). *Spectrometric Identification of Organic Compounds*, p. 114. John Wiley & Sons, New York.
[14] JCPDS, International Centre for Diffraction Data. CD-ROM 1998: CdS – file 41-1049; Cd_3OSO_4 – file 25-0113; CdO – file 5-0640; ZnS – file 361451; ZnO – file 36-1451; CuO – file 41-0254; Cu_2OSO_4 – file 13-0189.
[15] M. Chandrasekharan, M.R. Udupa and G. Aravamudan (1973). *Inorg. Chim. Acta*, **7**, 88.
[16] K. Nakamoto (1986). *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, p. 342, 4th Edn. Willey Interscience Publication, New York, Tokyo, Sydney, Toronto.