Journal of Thermal Analysis and Calorimetry, Vol. 79 (2005) 509–514

NANOPARTICLES OF ZINC COMPOUNDS OBTAINED BY THERMOOXIDATIVE DEGRADATION

A. Dumbrava[1*]*, B. Jurca*[2]*, V. Ciupina*[3]*, E. Segal*[2] *and M. Brezeanu*[4]

[1]Department of Chemistry, Faculty of Physics and Chemistry, 'Ovidius' University, 124 Mamaia Street, Constantza, Romania
[2]Department of Physical Chemistry, Faculty of Chemistry, University of Bucharest, 4-12 Elisabeta Blvd., Bucharest, Romania
[3]Department of Physics, Faculty of Physics and Chemistry, 'Ovidius' University, 124 Mamaia Street, Constantza, Romania
[4]Department of Inorganic Chemistry, Faculty of Chemistry, University of Bucharest, 23 Dumbrava Rosie Street, Bucharest, Romania

Nanocrystalline zinc compounds were obtained by thermooxidative degradation of zinc complexes. There are presented the conditions of synthesis and results in the characterisation (chemical analysis, thermal analysis) for two complex compounds of zinc: $[Zn(phen)(S_2O_3)(H_2O)]\cdot 2H_2O$ and $[Zn(phen)_2(H_2O)_2][Zn(phen)(S_2O_3)_2]\cdot 4H_2O$. On the basis of transmission electron microscopy (TEM) the complex sulfide and zinc oxide (prepared by controlled thermal decomposition of these compounds) may be included in the nanomaterials category.

Keywords: *complex compounds, nanoparticles, phenantroline, TEM, thermal analysis, thermooxidative degradation, thiosulfate, zinc*

Introduction

The study of complex compounds with ligands having sulfur as atom donor and/or sulfide ions as ligands is still of topical interest because of biological importance, interesting structural chemistry and possibility of using as catalyser. A general procedure for the synthesis of metal–sulfur complexes does not exist. However, such very different reagents, for instance, H_2S, S_8, S_x^{2-}, SCN^-, $S_2O_3^{2-}$, RNSNR or RSH, may be the precursors of sulfide ligands. Very little is known about the reaction pathways [1, 2].

In order to obtain complex compounds, which can be precursors for complex sulfides of zinc, it was studied the system:

$Zn(CH_3COO)_2$:$Na_2S_2O_3$:1,10-phenanthroline (phen)

From this system there were separated two compounds, $[Zn(phen)(S_2O_3)(H_2O)]\cdot 2H_2O$ and $[Zn(phen)_2(H_2O)_2][Zn(phen)(S_2O_3)_2]\cdot 4H_2O$.

Experimental

Materials

All the chemicals used for the present study were purchased from commercial sources and used without further purification.

Syntheses

Synthesis of the complex $[Zn(phen)(S_2O_3)(H_2O)]\cdot 2H_2O$ (**1**)

Complex **1** was obtained as follows: in an aqueous solution containing 1.1 g (5 mmol) $Zn(CH_3COO)_2\cdot 2H_2O$ in 100 mL water were added 0.99 g (5 mmol) 1,10-phenanthroline and 1.24 g (10 mmol) $Na_2S_2O_3\cdot 5H_2O$ and the resulted solution was heated under continuous stirring for 2 h. It was separated a white powder, which was filtered and washed with hot water.

Elemental analysis found (calc.) for: $ZnC_{12}H_{14}N_2S_2O_6$, (**1**) Zn: 15.45% (15.81); S: 14.63% (15.57%); N: 6.98% (6.81%).

Synthesis of the complex $[Zn(phen)_2(H_2O)_2][Zn(phen)(S_2O_3)_2]\cdot 4H_2O$ (**2**)

Complex **2** was obtained as follows: in an aqueous solution containing 1.1 g (5 mmol) $Zn(CH_3COO)_2\cdot 2H_2O$ in 100 mL water were added 0.99 g (5 mmol) 1,10-phenanthroline and 1.24 g (10 mmol) $Na_2S_2O_3\cdot 5H_2O$ and the resulted solution was heated under continuous stirring for 2 h. It was separated a white powder, which was filtered (**1**) and the resulted solution was kept to cool. There were obtained white crystals, which were filtered and washed with cold water.

Elemental analysis found (calc.) for: $Zn_2C_{24}H_{28}N_4S_4O_{12}$ (**2**) Zn: 13.75% (12.97%); S: 13.41% (12.77%); N: 8.78% (8.38%).

---

[*] Author for correspondence: adumbrava@univ-ovidius.ro

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

Synthesis of the complex $[Zn_2(phen)_2(S)]SO_4$ (**3**)

Complex **3** was obtained as follows: 2.05 g (5 mmol) of **1** were heated in an oven at 603 K and kept for 15 min at this temperature. The resulted powder was cooled in the exsiccator.

Elemental analysis found (calc.) for: $Zn_2C_{24}H_{16}N_2S_2O_4$ (**3**) Zn: 20.38% (21.04%); S: 9.76% (10.36%); N: 9.45% (9.06%).

Physical measurements

The IR (as KBr pellets) spectra were recorded on Bruker Vector 22 spectrometer, in the range of 400–4000 cm^{-1}. The heating curves have been recorded using a Paulik–Paulik–Erdey Q 1500 D derivatograph, in static air atmosphere, with α-Al_2O_3 as the inert reference compound, at various heating rates (from 2.5 to 10 K min^{-1}), in the range 293–1273 K. The sample masses were between 90–100 mg. The TEM were made with on the Philips CM 120 transmission electron microscope operated at 100 kV, with 2Å resolution.

Results and discussion

The research of above system had in view the contribution of parameters like: molar ratio of components, temperature, time, value of pH, order of reactants adding, at the nature of synthesised compounds. There were established the conditions for obtaining the compounds:

1 $[Zn(phen)(S_2O_3)(H_2O)]\cdot 2H_2O$

2 $[Zn(phen)_2(H_2O)_2][Zn(phen)(S_2O_3)_2]\cdot 4H_2O$

Complex **2** is known in chemistry literature [3] but: (*i*) it was obtained using a different method of the method presented in this paper; (*ii*) it was not studied the capacity of complex to be a precursor for complex sulfide.

The results proved that the nature of obtained compound is the same, independent of the reaction conditions, which were changed in a large range. This behaviour indicates a great stability of the complex. The chemical analysis of compounds proved that hydrolysis of both (at room temperature or high temperature) does not occur.

The compounds obtained from studied system were characterised by chemical analysis, thermal analysis and IR spectra.

Thermal analysis

The thermal decomposition of complex **1** in the temperature range 293–1273 K, at a heating rate of 5 K min^{-1}, respective 2.5 K min^{-1}, occurs through four steps (Fig. 1):

- the first step (in the temperature range 353–398 K) is endothermic and consists of the elimination of uncoordinated water molecules:

$$\begin{aligned}&[Zn(phen)(S_2O_3)\cdot H_2O]\cdot 2H_2O_{(s)} \xrightarrow{388\ K}\\ &\xrightarrow{388\ K} [Zn(phen)(S_2O_3)\cdot H_2O]_{(s)}+2H_2O_{(g)}\end{aligned}\qquad(1)$$

$\Delta m_{calc.}$=8.76%; Δm_{found}=9.95%. The temperature written above the arrow corresponds to the maximum decomposition rate as shown by the DTG curve;

- the second step (in temperature range 470–526 K) is endothermic too and consists in the elimination of coordinated water molecule:

$$\begin{aligned}&[Zn(phen)(S_2O_3)\cdot H_2O]_{(s)} \xrightarrow{503\ K}\\ &\xrightarrow{503\ K} [Zn(phen)(S_2O_3)]_{(s)}+H_2O_{(g)}\end{aligned}\qquad(2)$$

$\Delta m_{calc.}$=4.38%; Δm_{found}=5.07%;

- the third step (in temperature range 563–637 K) consists in the changing of thiosulfate ions into sulfide and sulfate ions:

$$\begin{aligned}&2Zn(phen)(S_2O_3)_{(s)}+O_{2(g)} \xrightarrow{601\ K}\\ &\xrightarrow{601\ K} Zn_2(phen)_2(S)(SO_4)_{(s)}+2SO_{2(g)}\end{aligned}\qquad(3)$$

$\Delta m_{calc.}$=11.68%; Δm_{found}=11.94%;

- the fourth step (in temperature range 723–927 K) is strong exothermic and consists in the oxidation of phenanthroline, the oxidation of sulfide ion to sulfate ion and the decomposition of zinc sulfate in zinc oxide [4].

The overall equation is [5]:

$$\begin{aligned}&Zn_2(phen)_2(S)(SO_4)_{(s)}+33O_{2(g)} \xrightarrow{845\ K}\\ &\xrightarrow{845\ K} 2ZnO_{(s)}+24CO_{2(g)}+\\ &+8H_2O_{(g)}+4NO_{2(g)}+2SO_{2(g)}\end{aligned}\qquad(4)$$

$\Delta m_{calc.}$=55.47%; Δm_{found}=51.25%.

The transformation of thiosulfate ion in coordinated sulfide ion confirms the coordination of thiosulfate in complex **1** through sulfur atom.

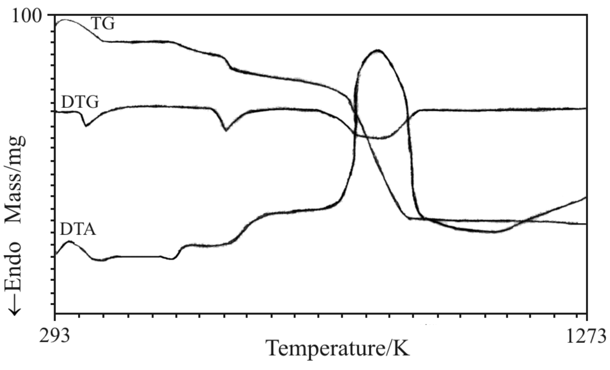

Fig. 1 Thermal curves for complex **1**

The thermal decomposition of complex **2** in the temperature range 293–1273 K, at a heating rate of 5 K min^{-1}, occurs through four steps (Fig. 2):

- the first step (in the temperature range 313–373 K) consists of elimination uncoordinated water molecules:

$$[Zn(phen)_2(H_2O)_2][Zn(phen)(S_2O_3)_2]\cdot 4H_2O_{(s)} \rightarrow$$
$$\rightarrow [Zn(phen)_2(H_2O)_2][Zn(phen)(S_2O_3)_2]_{(s)}+$$
$$+4H_2O_{(g)} \qquad (5)$$

$\Delta m_{\text{calc.}}=7.18\%$; $\Delta m_{\text{found}}=6.75\%$;

- the second step (in temperature range 458–523 K) consists in elimination of coordinated water molecules:

$$[Zn(phen)_2(H_2O)_2][Zn(phen)(S_2O_3)_2]_{(s)} \rightarrow$$
$$\rightarrow [Zn(phen)_2][Zn(phen)(S_2O_3)_2]_{(s)}+2H_2O_{(g)} \quad (6)$$

$\Delta m_{\text{calc.}}=3.59\%$; $\Delta m_{\text{found}}=3.93\%$;

- the third step (in temperature range 523–708 K) consists in changing thiosulfate ions into sulfide and sulfate ions:

$$[Zn(phen)_2][Zn(phen)(S_2O_3)_2]_{(s)}+O_{2(g)} \rightarrow$$
$$\rightarrow [Zn(phen)_2][Zn(phen)(S)(SO_4)]_{(s)}+2SO_{2(g)} \quad (7)$$

$\Delta m_{\text{calc.}}=9.58\%$; $\Delta m_{\text{found}}=10.12\%$;

- the fourth step (in temperature range 748–973 K) is strong exothermic and consists in oxidation of phenanthroline, oxidation of sulfide ion to sulfate ion and decomposition of zinc sulfate in zinc oxide.

$$[Zn(phen)_2][Zn(phen)(S)(SO_4)]_{(s)}+49O_{2(g)} \rightarrow 2ZnO_{(s)}+$$
$$+36CO_{2(g)}+12H_2O_{(g)}+6NO_{2(g)}+2SO_{2(g)} \qquad (8)$$

$\Delta m_{\text{calc.}}=61.47\%$; $\Delta m_{\text{found}}=56.22\%$.

The final product resulted from thermal decomposition of complex **2** is ZnO [6].

According with thermal analysis, compound **3** was obtained by controlled heating of complex **1** at 601 K. Due of chemical analysis the minimal formula for **3** is $[Zn_2(phen)_2(S)]SO_4$. The presence of uncoordinated sulfate ion is proved by IR spectrum.

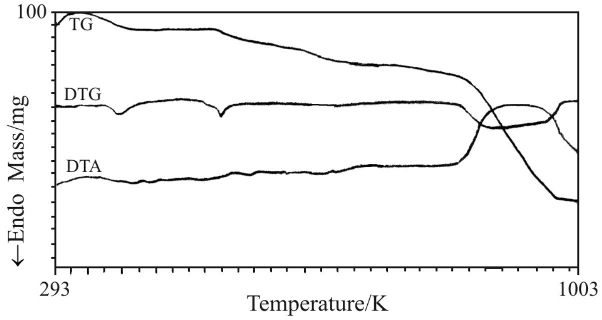

Fig. 2 Thermal curves for complex **2**

IR spectra

IR spectra for compounds **1** and **3** in range 400–4000 cm^{-1} were discussed according to [7, 8].

By the examination of IR spectral data (Table 1) it results the following remarks:

- in spectrum of complex **1** are present bands assigned of thiosulfate ion and phenanthroline. In spectrum of complex **3** are presented bands assigned to phenanthroline. The fact that bands assigned to thiosulfate are not present in spectrum of **3** is due to the disappearance of thiosulfate anion;
- the movement of bands assigned to the vibration mode ν(C=N) to higher energies suggests that phenathroline is coordinated through nitrogen atoms in both complexes;
- the bands $\nu_s(SO_3)$ and $\nu_a(SO_3)$ are moved to higher energies in spectrum of **1**, suggesting that thiosulfate ion is coordinated as monodentate ligand through sulfur or as bridging sulfur ligand [9, 10];
- a new band at about 1100 cm^{-1}, the most intense in spectrum of complex **3**, can be assigned to the vibration mode $\nu_3\,(SO_4^{2-})$ of sulfate ion. The presence of uncoordinated sulfate ion is confirmed by the band at about 620 cm^{-1} assigned to vibration mode $\nu_4\,(SO_4^{2-})$;
- in spectrum of complex **1** a strong, broad band at about 3400 cm^{-1} reveals presence of water molecules as coordination and/or crystallisation water. The presence of water is also demonstrated by the band at about 1600 cm^{-1} due to the vibration mode $\delta(H_2O)$ in the spectrum of complex **1**.

Having in view the characteristic tetrahedral stereochemistry of zinc, for complex **1** can be proposed the most probable formula as in Fig. 3. The IR spectra can't make the difference between the coordination of thiosulfate ion as monodentate ligand through sulfur atom or as bridging sulfur ligand. A possible formula is that in which the thiosulfate anion is monodentate ligand through sulfur, in the fourth coordination site being a water molecule.

On the basis of all chemical and physico-chemical data, the most probable formula for complex **3** is dimeric, with bridging sulfide ligand (Fig. 4).

Electron microscopy

The size of primary nanoparticles can be determined from imaging by TEM. This technology is more direct than X-ray line broadening and less likely to be affected by experimental errors and/or other properties of the particles such as strain or a distribution in the size of lattice parameter [11]. Figure 5 depicts the bright field TEM micrographs of $[Zn_2(phen)_2(S)]SO_4$ and ZnO, respectively. The figures indicate that most parti-

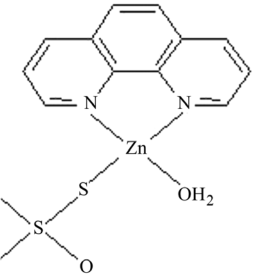

Fig. 3 The most probable formula proposed for complex **1**, $[Zn(phen)(S_2O_3)(H_2O)]\cdot 2H_2O$

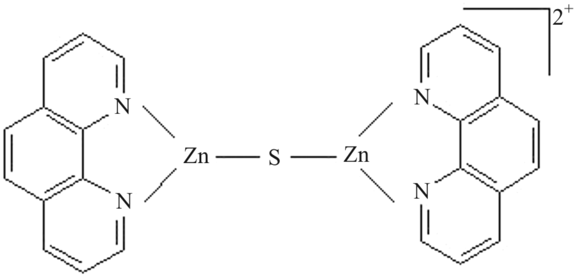

Fig. 4 The most probable formula proposed for complex **3**, $[Zn_2(phen)_2(S)]SO_4$

cles are fine and spherical. As shown, the particles of ZnO are nearly uniform and the diameters are in range of 20–50 nm. For the complex sulfide most particles have diameters in range of 20–30 nm, the number of particles with diameters above 100 nm being small over that of particles with diameters below 100 nm.

The morphology and mean diameter are estimated using TEM micrograph (Figs 5 and 6). Figure 6 presents lognormal distribution curves for mean diameter. The lognormal function used for fit the experimental curves is given by:

$$y = A\mathrm{e}^{-\frac{\ln^2(x/x_c)}{2w^2}}$$

where A is an arbitrary constant related to particle number, x_c represents the distribution maximum and w is strong correlated with particle diameter dispersion.

From Fig. 6 it can be seen that, for ZnO, size distribution of particles is narrowly dispersed.

The crystalline structure for ZnO, obtained from electron diffraction, is hexagonal (P63mc), of wurtzite type, with a=0.3242 nm, c=0.5176 nm.

Table 1 Infrared spectra (cm^{-1})

$phen\cdot H_2O$	$Na_2S_2O_3\cdot 5H_2O$	$[Zn(phen)(S_2O_3)\cdot H_2O]\cdot 2H_2O$ (**1**)	$[Zn_2(phen)_2(S)]\cdot SO_4$ (**3**)	Assignments
400 w 438 w	–	407 w	422 vw	ν ring, ν(M–N)
–	544 s	526 m	–	$\delta_s(SO_3)$
–	–	–	617 m	$\nu_4(SO_4^{2-})$
622 m	–	–	–	ν(C–C)
–	668 s	642 s	–	$\delta_a(SO_3)$
736 vs	–	726 s	725 vs	ν(C–H)
777 w	–	771 w	776 w	ν(C–H)
850 vs	–	854 s	850 s	ν(C–H)
–	1003 s	1009 vs	–	$\nu_s(SO_3)$
1089 m	–	1107 m	1103 m	β(C–H)
–	–	–	1117 s	$\nu_3(SO_4^{2-})$
–	1123 s 1167 s	1144 s 1183 s	–	$\nu_a(SO_3)$
1336 w	–	1343 vw	1343 vw	ν(C–C)
1420 vs	–	1426 m	1427 m	ring vibrations
1503 s	–	1517 m	1517 m	ν(C=N)
1550 w 1591 m	–	1583 m	1582 w	ν(C=N)
1614 w 1648 m	1657 m	1627 w	–	$\delta(H_2O)$
2983 w 3024 w 3068 m	–	3064 m	2856 vw 2930 w 3063 w	ν(C–H)
3418 s, broad	3452 vs, broad	3450 s, broad	–	ν(O–H)

vs – very strong, s – strong, m – medium, w – weak, vw – very weak

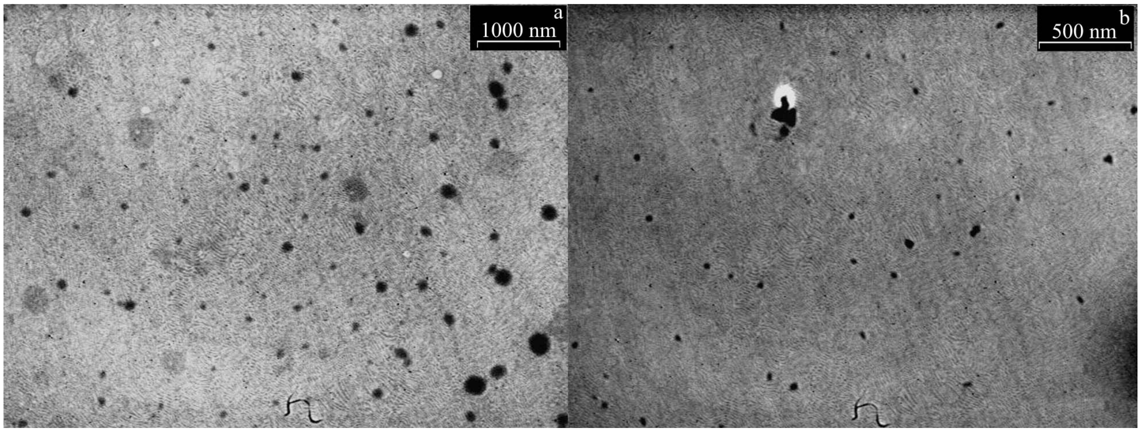

Fig. 5 The TEM micrographs of nanocrystalline powders: a – $[Zn_2(phen)_2(S)]SO_4$, b – ZnO

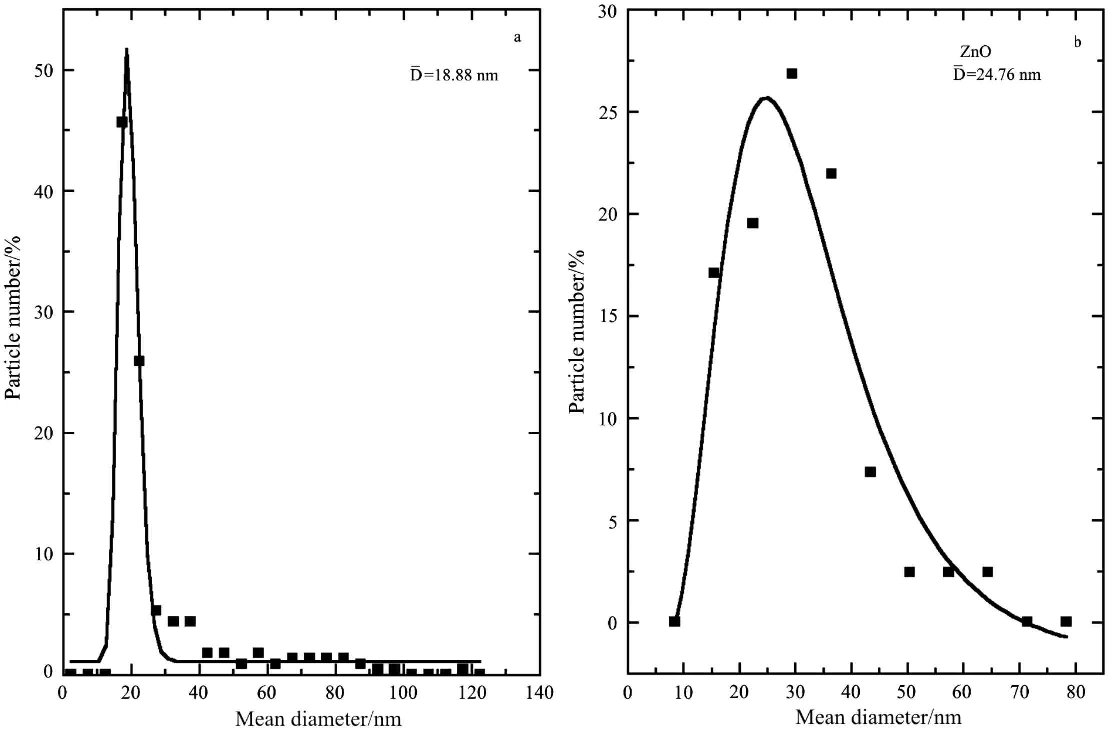

Fig. 6 Mean particle size and particle distribution of nanocrystalline powders: a – $[Zn_2(phen)_2(S)]\cdot SO_4$, b – ZnO. Results were obtained from TEMs

Conclusions

This paper described:

- the synthesis and characterisation of two complexes of zinc with 1,10-phenanthroline and thiosulfate anion, having formulas $[Zn(phen)(S_2O_3)(H_2O)]\cdot 2H_2O$ and $[Zn(phen)_2(H_2O)_2][Zn(phen)(S_2O_3)_2]\cdot 4H_2O$;
- the syntheses of complex sulfide $[Zn_2(phen)_2(S)]SO_4$ by thermal decomposition of $[Zn(phen)(S_2O_3)(H_2O)]\cdot 2H_2O$.

On the basis of electron microscopy the complex sulfide and ZnO, obtained as final product in thermal decomposition of $[Zn(phen)(S_2O_3)(H_2O)]\cdot 2H_2O$ can be included in the category of nanomaterials.

Supplementary material

Additional material consists of table with ID particle, ID class, diameter mean, area and perimeter for each particle analysed.

References

1 A. Müller and E. Diemann, Sulfides, in Comprehensive Coordination Chemistry, Pergamon Press, Oxford 1987.
2 L. Patron, O. Carp, I. Mindru, M. Pascu, N. Stanica, V. Ciupina, E. Segal and M. Brezeanu, J. Therm. Anal. Cal., 72 (2003) 271.
3 R. Baggio, S. Baggio, M. I. Pardo and M. T. Garland, Acta Cryst., C52 (1996) 820.
4 P. Pascal, Nouveau traité de chimie minérale, Masson et Cie, Paris 1962.
5 Z. Gabelica, Ann. Soc. Sci. Bruxelles, 89 (1975) 149.
6 E. Szunyogová, K. Györyová, J. Kovásová and E. Juhászová, J. Therm. Anal. Cal., 71 (2003) 967.
7 K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley, New York 1986.
8 A. T. Balaban, M. Banciu and I. Pogany, Aplicatii ale metodelor fizice in chimia organica, Editura Stiintifica si Enciclopedica, Bucuresti 1983.
9 Z. Gabelica, Bull. Soc. Roy. Scient. Liège, 44 (1975) 644.
10 Z. Gabelica, Ann. Soc. Scient. Brux., T91 (1977) 243.
11 Y. Wang, C. Ma, X. Sun and H. Li, Inorg. Chem. Com., 5 (2002) 751.