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SYNTHESIS OF CADMIUM COMPLEX SULFIDES NANOPARTICLES BY THERMAL DECOMPOSITION*

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The paper presents the conditions of synthesis and results in the characterisation (chemical analysis, thermal analysis, kinetic of decomposition) for two complex compounds of cadmium: $[Cd(S_2O_3)phen]\cdot H_2O$ and $[Cd(S_2O_3)phen_2]\cdot 2H_2O$. The obtained complexes were used as precursors for complex sulfides by controlled thermal decomposition. On the basis of transmission electron microscopy (TEM) the complex sulfides may be included in the nanomaterials category.

Keywords: *cadmium, complex sulfide, nanoparticles, phenanthroline, thermal analysis, thiosulfate*

Introduction

In last years nanomaterials have received a great attention for their potential applications (biology, chemical technology, medicine, etc.). The chemical and physical properties of nanostructured materials (which are characterised by at least one dimension in nanometre range) can significantly differ from those of the atomic molecular and the bulk materials with the same composition [1, 2].

Complex compounds which contain ligands having sulfur as donor atom and especially complex sulfides are interesting because: (*i*) can be used as model compounds, (*ii*) have interesting stereochemistry, (*iii*) can be used as catalysers and (*iv*) have biological importance. 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 [3]. Complex sulfides can be obtained by different methods from complexes that have ligands with sulfur as atom donor [4, 5].

The aim of our study is to obtain nanoparticles of complex sulfides by thermal decomposition of cadmium complexes having coordinated thiosulfate as generator of sulfide ion.

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

$$Cd(CH_3COO)_2{:}Na_2S_2O_3{:}1,10\text{-phenanthroline (phen)}$$

From this system there were separated two compounds, $[Cd(S_2O_3)phen]\cdot H_2O$ and $[Cd(S_2O_3)phen_2]\cdot 2H_2O$. By thermooxidative degradation of these complexes there were obtained nanoparticles of two complex sulfides, $[Cd_2(phen)_2(S)]SO_4$ and $[Cd_2(phen)_4(S)]SO_4$.

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 $[Cd(S_2O_3)phen]\cdot H_2O$ (**1**)

Complex **1** was obtained as follows: 0.99 g (5 mmol) 1,10-phenanthroline$\cdot H_2O$ and 2.48 g (10 mmol) $Na_2S_2O_3\cdot 5H_2O$ were added into an aqueous solution containing 1.33 g (5 mmol) $Cd(CH_3COO)_2\cdot 2H_2O$ in 100 cm^3 water and the resulted solution was heated under continuous stirring for two hours. It was separated a yellowish powder, which was filtered and washed with hot water. Anal. Found: Cd, 26.22; S, 15.47; N, 7.51. Calc. for $CdC_{12}H_{10}N_2S_2O_4$: Cd, 26.54; S, 15.16; N, 6.63.

Synthesis of the complex $[Cd(S_2O_3)phen_2]\cdot 2H_2O$ (**2**)

Complex **2** was obtained as follows: 0.99 g (5 mmol) 1,10-phenanthroline$\cdot H_2O$ and 6.20 g (25 mmol) $Na_2S_2O_3$

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$\cdot 5H_2O$ were added into an aqueous solution containing 1.33 g (5 mmol) $Cd(CH_3COO)_2\cdot 2H_2O$ in 100 cm^3 water and the resulted solution was heated under continuous stirring for two hours. It was separated a yellowish powder, which was filtered and washed with hot water. Anal. Found: Cd, 18.24; S, 10.01; N, 9.62. Calc. for $CdC_{24}H_{20}N_4S_2O_5$: Cd, 18.06; S, 10.32; N, 9.03.

Synthesis of the complex $[Cd_2(phen)_2(S)]SO_4$ (**3**)

Complex **3** was obtained as follows: 2.11 g (5 mmol) of **1** were heated in an oven at 551 K and kept for 15 min at this temperature. The resulted powder was cooled in the exsiccator. Anal. Found: Cd, 31.54; S, 9.23; N, 8.61. Calc. for $Cd_2C_{24}H_{16}N_4S_2O_4$: Cd, 31.46; S, 8.99; N, 7.86.

Synthesis of the complex $[Cd_2(phen)_4(S)]SO_4$ (**4**)

Complex **4** was obtained as follows: 3.1 g (5 mmol) of **2** were heated in an oven at 510 K and kept for 15 min at this temperature. The resulted powder was cooled in the exsiccator. Anal. Found: Cd, 20.69; S, 6.67; N, 10.97. Calc. for $Cd_2C_{48}H_{32}N_8S_2O_4$: Cd, 20.89; S, 5.97; N, 10.45.

The elemental chemical analyses were performed by usual micromethods.

Physical measurements

The IR spectra of pellets with KBra were recorded on Bruker Vector 22 spectrometer, in the range of 400–4000 cm^{-1}. The DTA-TG curves have been recorded using a Paulik–Paulik–Erdey Q 1500 D derivatograph, in static air atmosphere, with α-Al_2O_3 as an inert reference compound, at various heating rates (from 1.25 to 10 K min^{-1}), in the range 293–1273 K. The sample masses were between 90–100 mg. The thermoanalytical data have been used in order to evaluate the decomposition kinetic parameters by three integral methods: Coats–Redfern [6, 7], Flynn–Wall [8, 9] (for constant heating rate) and Urbanovici–Segal [10, 11] who modified Coats–Redfern method. For automatic processing of the data the Versatile program was used [12–14]. The TEM was made on the Phillips CM 120 ST transmission electron microscope using an accelerating voltage of 100 kV, with 2 Å resolution.

Results and discussion

The first step of our research was the synthesis of new cadmium complexes having thiosulfate anion and 1,10-phenanthroline as ligands, which can be used as precursors for complex sulfides.

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

1	$[Cd(S_2O_3)phen]\cdot H_2O$
2	$[Cd(S_2O_3)phen_2]\cdot 2H_2O$

Complex **1** is known in literature [15] but: (*i*) it was obtained using a different method than 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 that were changed, in a large range. This behaviour indicates a great stability of the complex. The chemical analysis of compounds proved that it does not occur hydrolysis of both (at room temperature or high temperature).

The compounds obtained from the studied system were characterised by chemical analysis, DTA-TG and IR methods.

The second step of research was the synthesis of complex sulfides by thermooxidative degradation. The compounds obtained by thermooxidative degradation were characterised by chemical analysis, IR spectra and TEM.

Thermal decomposition and kinetic studies

Thermal decomposition of complex $[Cd(S_2O_3)phen]\cdot H_2O$ (**1**) in the temperature range 293–1273 K, at a heating rate of 10, 5, 2.5, respectively, 1.25 K min^{-1}, occurs through four steps (Fig. 1):

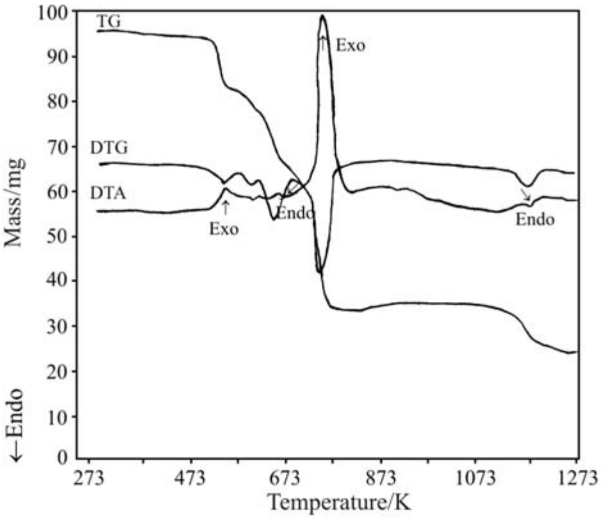

Fig. 1 TG, DTG and DTA curves for complex $[Cd(S_2O_3)phen]\cdot H_2O$ (**1**) at a heating rate of 5 K min^{-1}

- the first step (in the temperature range of 313–423 K) is endothermic and consists in elimination of uncoordinated water molecule:

$$[Cd(S_2O_3)phen]\cdot H_2O_{(s)} \xrightarrow{418\ K} [Cd(S_2O_3)phen]_{(s)}+H_2O_{(g)} \quad (1)$$

$\Delta m_{calc.}$=4.26%; Δm_{found}=4.04%;

The temperature written above the arrow corresponds to the maximum decomposition rate as shown by the DTG curve;

- the second step (in the temperature range of 518–573 K) is exothermic and consists in changing thiosulfate ions into sulfide and sulfate ions. This kind of thermal decomposition for sulfate ion is known from literature [16].

$$2[Cd(S_2O_3)phen]_{(s)}+O_{2(g)} \xrightarrow{551\ K} Cd_2(phen)_2(S)(SO_4)_{(s)}+2SO_{2(g)} \quad (2)$$

$\Delta m_{calc.}$=11.37%; Δm_{found}=12.97%;

- the third step (in the temperature range of 617–699 K) is endothermic and consists in loosing of a phenanthroline molecule:

$$Cd_2(phen)_2(S)(SO_4)_{(s)} \xrightarrow{666\ K} Cd_2(phen)(S)(SO_4)_{(s)}+phen_{(g)} \quad (3)$$

$\Delta m_{calc.}$=21.33%; Δm_{found}=19.87%;

- the fourth step (in the temperature range of 699–825 K) is strongly exothermic and consists in oxidation of phenanthroline and obtaining of cadmium sulfide and cadmium sulfate. Above 717 K cadmium sulfide is decomposed in elements and metallic cadmium can be oxidised to cadmium oxide. In the presence of SO_2 is possible the reaction [17]:

$$CdS+2SO_2 \longrightarrow CdSO_4+2S$$

Elemental sulfur can be oxidised to SO_2.

The most probable reaction in these conditions is:

$$3/2Cd_2(phen)(S)(SO_4)_{(s)}+26O_{2(g)} \xrightarrow{764\ K} 2CdO_{(s)}+ CdSO_{4(s)}+18CO_{2(g)}+6H_2O_{(g)}+3NO_{2(g)}2SO_{2(g)} \quad (4)$$

$\Delta m_{calc.}$=26.38%; Δm_{found}=25.56%.

The values of kinetic parameters obtained for the reaction (4) are presented in Table 1.

Using the equations of Arrhenius and Eyring simultaneously, the values of change of entropy for the activated complex formation from the reagent ($\Delta S^{\neq}$) can be calculated according to the formula:

$$\Delta S = R\ln\frac{Zh}{\chi e k_B T_p}$$

where χ is the transmission factor, which is unity for monomolecular reaction, k_B is the Boltzmann constant, h is the corresponding Plank constant, e=2.7183 is the Neper number and T_p is the peak temperature from the DTG curve. For the first complex $\Delta S^{\neq}$= 142.0 J mol^{-1} K^{-1}. The positive value of $\Delta S^{\neq}$ shows that the activated complex is less organized than the reagent.

Table 1 Kinetic parameters value for reaction (4) in thermal decomposition of complex **1**

Method	CR	FW	US
Z/s^{-1}	1.14·10^{21}	6.10·10^{21}	2.42·10^{21}
E/kJ mol^{-1}	340	336	345
n	1.6	1.6	1.6
r	–0.9951	–0.9954	–0.9952

Z – pre-exponential factor, E – activation energy, n – apparent order, r – correlation coefficient of the linear regression; CR – Coats–Redfern, FW – Flynn–Wall, US – Urbanovici–Segal

According to the formulas:

$$\Delta H^{\neq}=E-RT_p$$

and

$$\Delta G^{\neq}=\Delta H^{\neq}-T_p\Delta S^{\neq}$$

the values of $\Delta H^{\neq}$ (333.7 kJ mol^{-1}) and $\Delta G^{\neq}$ (225.2 kJ mol^{-1}) were calculated respectively at the peak temperature T_p [18, 19].

- the fifth step (in the temperature range of 1135–1250 K) consists in decomposition of cadmium sulfate and cadmium oxide (which is instable at temperatures above 1223 K), with formation of metallic cadmium:

$$2CdO_{(s)}+CdSO_{4(s)} \xrightarrow{1243\ K} 3Cd_{(s)}+SO_{2(g)}+2O_{2(g)} \quad (5)$$

$\Delta m_{calc.}$=10.11%; Δm_{found}=11.23%.

The decomposition of thiosulfate ion with formation coordinated sulfide ion, confirms the coordination of thiosulfate through sulfur atom in $[Cd(phen)(S_2O_3)]\cdot H_2O$.

The thermal decomposition of complex $[Cd(S_2O_3)phen_2]\cdot 2H_2O$ (**2**) in the temperature range of 293–1273 K, at the heating rate of 5 K min^{-1}, occurs through four steps:

- the first step (in the temperature range of 343–408 K) consists of elimination uncoordinated water molecules, in an endothermic process:

$$[Cd(phen)_2(S_2O_3)]\cdot 2H_2O_{(s)} \longrightarrow [Cd(phen)_2(S_2O_3)]_{(s)}+2H_2O_{(g)} \quad (6)$$

$\Delta m_{calc.}$=5.82%; Δm_{found}=5.61%;

- the second step (in the temperature range of 477–532 K), exothermic, consists in changing thiosulfate ions into sulfide and sulfate ions:

$$2Cd(phen)_2(S_2O_3)_{(s)}+O_{2(g)} \xrightarrow{510\ K} Cd_2(phen)_4(S)(SO_4)_{(s)}+2SO_{2(g)} \quad (7)$$

$\Delta m_{\text{calc.}}=7.74\%$; $\Delta m_{\text{found}}=7.24\%$.

The presence of coordinated sulfide ion is a proof of thiosulfate coordination through sulfur atom;

- the third step (in the temperature range of 572–668 K), endothermic, consists in loosing of two phenanthroline molecules, without burning:

$$Cd_2(phen)_4(S)(SO_4)_{(s)}\xrightarrow{634\,K}$$
$$Cd_2(phen)_2(S)(SO_4)_{(s)}+2phen_{(g)} \qquad (8)$$

$\Delta m_{\text{calc.}}=29.03\%$; $\Delta m_{\text{found}}=29.59\%$;

- the fourth step (in the temperature range of 668–820 K) is strongly exothermic and consists in oxidation of phenanthroline:

$$3/2Cd_2phen_2(S)(SO_4)_{(s)}+50O_{2(g)}\xrightarrow{761\,K}2CdO_{(s)}+$$
$$+CdSO_{4(s)}+36CO_{2(g)}+12H_2O_{(g)}+6NO_{2(g)}+2SO_{2(g)} \quad (9)$$

$\Delta m_{\text{calc.}}=31.47\%$; $\Delta m_{\text{found}}=30.53\%$;

- the fifth step (in the temperature range of 1147–1244 K), consists in decomposing of cadmium sulfate and cadmium oxide and obtaining of metallic cadmium:

$$2CdO_{(s)}+CdSO_{4(s)}\xrightarrow{\quad}3Cd_{(s)}+SO_{2(g)}+2O_{2(g)} \quad (10)$$

$\Delta m_{\text{calc.}}=8.58\%$; $\Delta m_{\text{found}}=9.08\%$.

The final product resulted from thermal decomposition of complex **2** is metallic cadmium.

According the results of thermal decomposition, compounds **3** and **4** were obtained by controlled heating of complex **1** at 551 K, respective of complex **2** at 510 K. On the basis of chemical analysis the minimal formula for **3** is $[Cd_2(phen)_2(S)]SO_4$ and for **4** is $[Cd_2(phen)_4(S)](SO_4)$. The presence of uncoordinated sulfate ion in both compounds is proved by IR spectra.

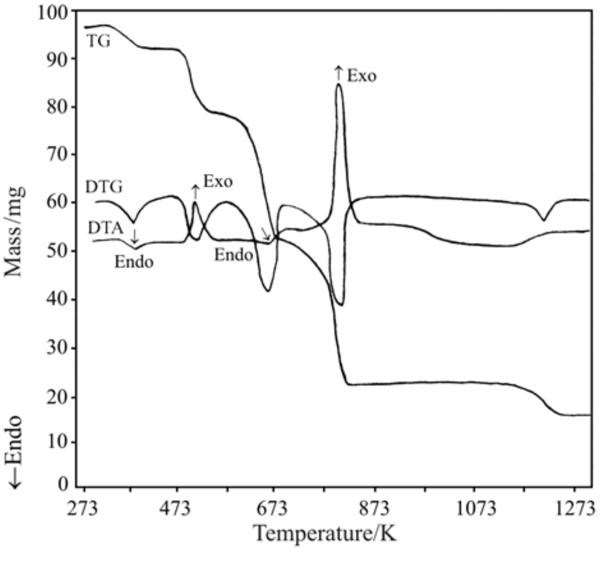

Fig. 2 DTA-TG curves for complex $[Cd(S_2O_3)phen_2]\cdot 2H_2O$ (**2**) at a heating rate of 5 K min^{-1}

IR spectra

IR spectra for compounds **1**–**4** in the range of 400–4000 cm^{-1} were discussed according to the literature data [20, 21].

From the examination of IR data (Table 2) the following conclusions result:

- in spectra of complexes **1** and **2** are found bands assigned of thiosulfate ion and phenanthroline. In spectra of complexes **3** and **4** are found bands assigned to phenanthroline. The fact that bands assigned to thiosulfate are not found in spectra of **3** and **4** is due to disappearance of thiosulfate anion;
- the movement of bands assigned to the vibration mode ν(C=N) to higher energies suggests that phenanthroline is coordinated through nitrogen atoms in both complexes;
- the band $\nu_s(SO_3)$ is moved to lower energy and the bands $\nu_a(SO_3)$ are split in two components in spectra of compounds **1** and **2**. This fact suggests that thiosulfate ion is coordinated as chelating bidentate ligand or bridging bidentate ligand through sulfur and oxygen [22, 23];
- the new band at about 1100 cm^{-1}, the most intense in spectra of complexes **3** and **4** 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 spectra of complexes **1** and **2** 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 confirmed by the band at about 1600 cm^{-1} due to the vibration mode $\delta(H_2O)$ in spectra of complexes **1** and **2**.

For complex $[Cd(phen)(S_2O_3)]\cdot H_2O$ (**1**) can be proposed the most probable formula as in Fig. 3, in which the thiosulfate anion is a chelating ligand. The presence of water molecule as hydration water, not as coordination water, as in [15], is demonstrated by thermal analysis.

On the basis of all chemical and physico-chemical data, the most probable formula for complex $[Cd(S_2O_3)phen_2]\cdot 2H_2O$ (**2**) is shown in Fig. 4.

For complex ions in compounds **3** and **4** the most probable formulas are shown in Figs 5 and 6, respectively.

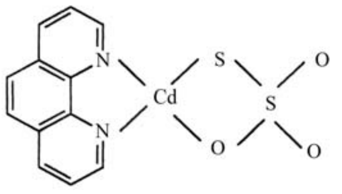

Fig. 3 The most probable formula proposed for complex $[Cd(phen)(S_2O_3)]\cdot H_2O$ (**1**)

Table 2 IR frequencies of phen·H_2O, $Na_2S_2O_3$·$5H_2O$, [Cd(S_2O_3)phen]·H_2O (**1**), [Cd(S_2O_3)$phen_2$]·$2H_2O$ (**2**), [$Cd_2$$(phen)_2$(S)]·$SO_4$ (**3**) and [$Cd_2$$(phen)_4$(S)]·$SO_4$ (**4**) (in cm^{-1})

phen·H_2O	$Na_2S_2O_3$·$5H_2O$	**1**	**2**	**3**	**4**	Assignments
–	428 m	421 w	417 w	419 s	418 w	ν(S–S)
–	544 s	541 m	539 w	–	–	$\delta_s(SO_3)$
–	–	–	–	619 s	620 s	$\nu_4(SO_4^{2-})$
622 m	–	638 vs	637 m	–	–	ν(C–C)
–	668 s	–	647 m 666 m	–	–	$\delta_a(SO_3)$
736 vs	–	724 s	727 vs	727 vs	730 s	ν(C–H)
777 w	–	781 w	777 w	778 w	779 w	ν(C–H)
850 vs	–	850 s	845 s	850 s	851 s	ν(C–H)
–	1003 s	1004 vs	996 vs	–	–	$\nu_s(SO_3)$
1089 m	–	1100 m	1096 m	1055 m	1054 m	β(C–H)
–	–	–	–	1116 vs	1116 vs	$\nu_3(SO_4^{2-})$
–	1123 s 1167 s	1135 vs 1153 vs 1182 vs	1120 vs 1141 vs 1185 vs	–	–	$\nu_a(SO_3)$
1128 m	–	–	–	–	–	ν(C–H)
1228 w	–	–	1221 vw	–	–	ν(C–N) aromatic
1336 w	–	1344 w	1344 w	1344 vw	1344 vw	ν(C–C)
1420 vs	–	1427 m	1428 s	1427 s	1427 s	Ring vibrations
1503 s 1550 w 1591 m	–	1515 m 1576 w	1514 m 1576 w 1591 w	1515 m 1574 w 1589 w	1515 m 1573 w 1589 w	ν(C=N)
1614 w 1648 m	1657 m	1619 w	1620 w	–	–	$\delta(H_2O)$
2983 w 3024 w 3068 m	–	3049 w	2990 vw 3048 w 3066 vw	3054 m	3052 m	ν(C–H)
3418 s, broad	3452 vs, broad	3447 m, broad	3423 s, broad	–	–	ν(O–H)

vs - very strong; s - strong; m - medium; w - weak, vw - very weak.

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 [24].

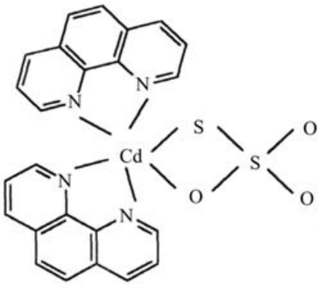

Fig. 4 The most probable formula proposed for complex [Cd(S_2O_3)$phen_2$]·$2H_2O$ (**2**)

Figures 7a and 8a depict the bright field TEM micrographs of [$Cd_2$$(phen)_2$(S)]$SO_4$ (**3**) and [$Cd_2$$(phen)_4$(S)]$SO_4$ (**4**), respectively. The figures indicate that most particles are nearly uniform, fine and spherical.

Particle sizes can be measured directly from TEM images. From Figs 7b and 8b it can be seen that, for both complexes size distribution of particles is narrowly dispersed with medium diameter of 5.59 nm

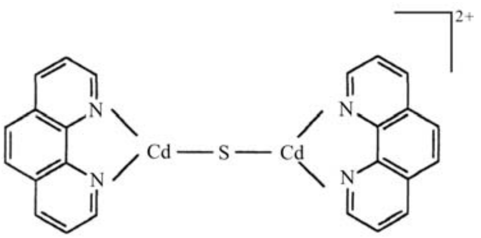

Fig. 5 The most probable formula proposed for complex ion in [$Cd_2$$(phen)_2$(S)]$SO_4$ (**3**)

for $[Cd_2(phen)_2(S)]SO_4$ (**3**) and 7.64 nm for $[Cd_2(phen)_4(S)]SO_4$ (**4**). Medium diameter of particle is evaluated by arithmetic mean of diameters measured at different angle (0, 15, 30, …180°), assuming lognormal distribution of nanoparticles. Experimental diameter measured from TEM micrograph was fitted with function given by:

$$y = y_0 + Ae^{\frac{\ln^2(x/x_c)}{2w^2}}$$

where A is a constant strongly related to particle count, x_c position of maximum, and w dispersion.

There were obtained values of 5.27 nm for $[Cd_2(phen)_2(S)]SO_4$ (**3**) and respective 7.20 nm for $[Cd_2(phen)_4(S)]SO_4$ (**4**) around of which there are distributed the medium diameters of particles.

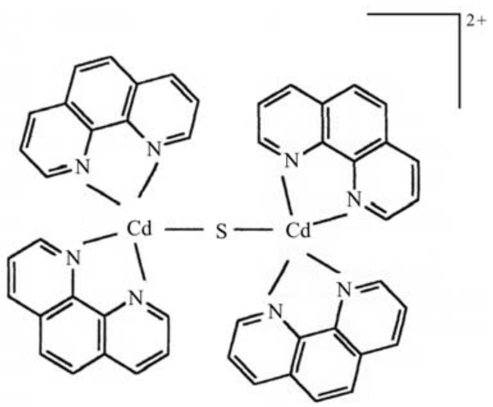

Fig. 6 The most probable formula proposed for complex ion in $[Cd_2(phen)_4(S)]SO_4$ (**4**)

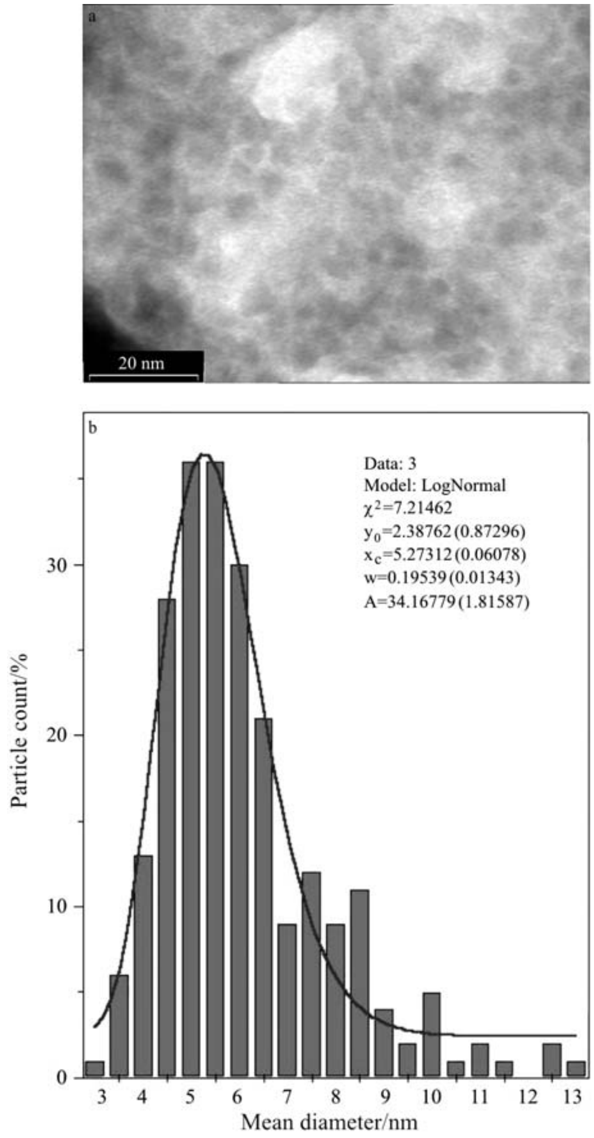

Fig. 7 a – The TEM image of $[Cd_2(phen)_2(S)]SO_4$ (**3**); b – Mean particle size and particle distribution for $[Cd_2(phen)_2(S)]SO_4$ (**3**)

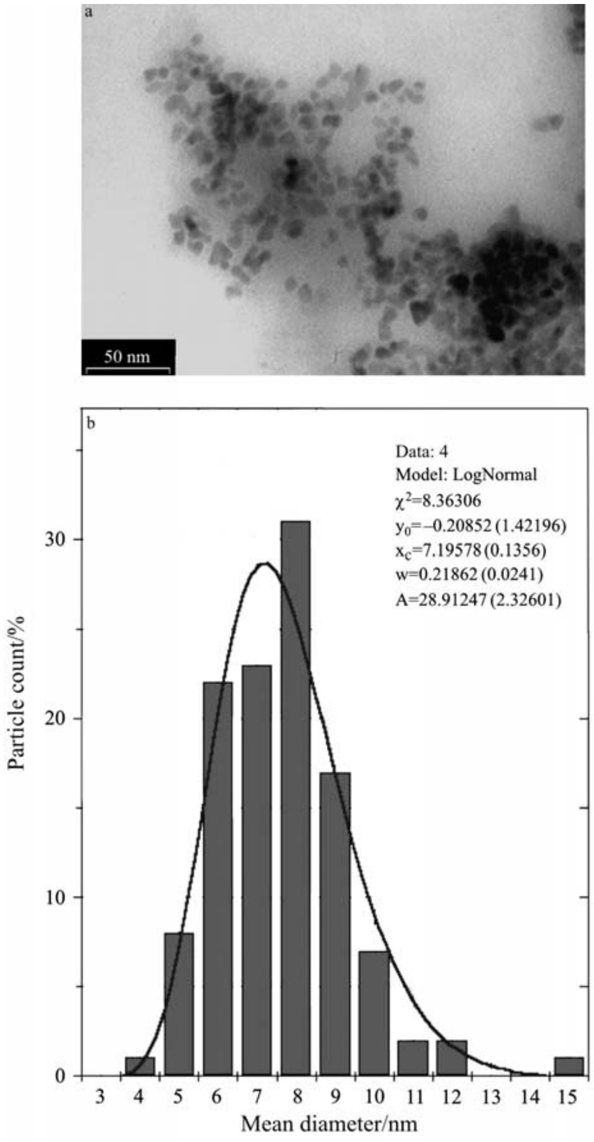

Fig. 8 a – The TEM image of $[Cd_2(phen)_4(S)]SO_4$ (**4**); b – Mean particle size and particle distribution for $[Cd_2(phen)_4(S)]SO_4$ (**4**)

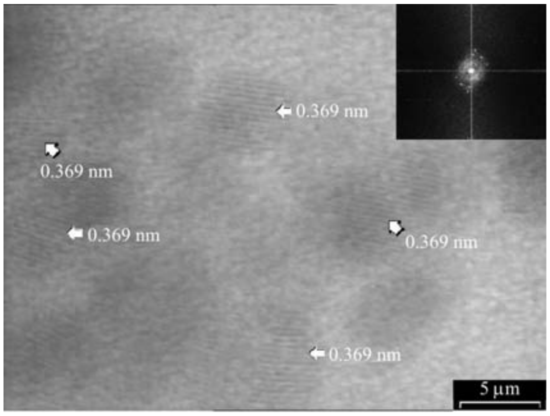

Fig. 9 HRTEM image of $[Cd_2(phen)_2(S)]SO_4$ (**3**)

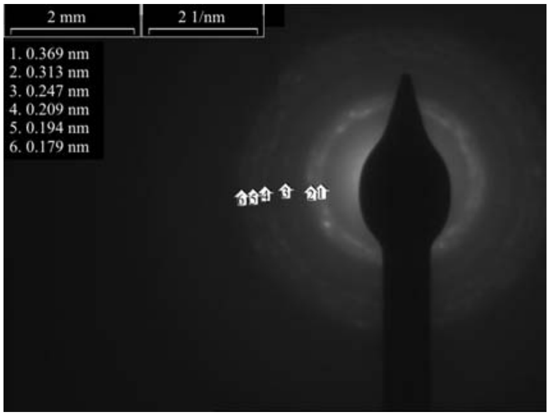

Fig. 10 SAED pattern obtained for $[Cd_2(phen)_2(S)]SO_4$ (**3**)

On the basis of particles dimensions both complex sulfides can be included in the nanoparticles category.

In the HRTEM (high-resolution electron microscopy) image for $[Cd_2(phen)_2(S)]SO_4$ (**3**) (Fig. 9) there can be observed nanodomains, which have dimensions distributed around 5.27 nm, as it was determinate by analysis of nanoparticles diameters.

From the SAED (selected area electron diffraction) pattern (Fig. 10) it were measured distances between planes for $[Cd_2(phen)_2(S)]SO_4$.

Conclusions

There were synthesised two new complex compounds of cadmium with 1,10-phenathroline and thiosulfate ion, having formulas $[Cd(S_2O_3)phen]\cdot H_2O$ (**1**), respective $[Cd(S_2O_3)phen_2]\cdot 2H_2O$ (**2**). The both compounds were characterised by chemical analysis, DTA-TG and IR methods. The authors proposed mechanism of decomposition for obtained complex compounds.

On the basis of the results of thermal decomposition, the complexes were used as precursors for complex sulfides. Thus, by thermooxidative degradation were obtained complexes $[Cd_2(phen)_2(S)]SO_4$ (**3**) and $[Cd_2(phen)_4(S)]SO_4$ (**4**), which were characterised by chemical analysis, IR spectra, TEM and HRTEM analyses.

The resulted complex sulfides of cadmium may be included in nanomaterials category, on the basis of medium diameter (5.59 nm for $[Cd_2(phen)_2(S)]SO_4$ and 7.64 nm for $[Cd_2(phen)_4(S)]SO_4$).

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