

## MIXED COMPLEX SULFIDES OF CADMIUM AND IRON WITH *p*-DIAMINOBENZENE AS LIGAND

Anca DUMBRAVĂ,<sup>a\*</sup> Victor CIUPINĂ,<sup>b</sup> Bogdan JURCĂ,<sup>c</sup> Gabriel PRODAN<sup>b</sup>  
and Maria BREZEANU<sup>\*\*</sup>

<sup>a</sup> Department of Chemistry, Ovidius University, 124 Mamaia Street, 900527 Constanța, Roumania

<sup>b</sup> Electron Microscopy Laboratory, Ovidius University, 1 Universitatii Street, 900470 Constanța, Roumania

<sup>c</sup> Department of Physical Chemistry, Faculty of Chemistry, 4-12 Elisabeta Bvd., University of Bucharest, 030018 Bucharest, Roumania

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Two complex sulfides of cadmium and iron having *p*-diaminobenzene as ligand,  $[\text{CdFe}_2(\text{pdab})_2(\text{S})_3(\text{H}_2\text{O})_6] \cdot \text{H}_2\text{O}$  and  $[\text{CdFe}(\text{pdab})_2(\text{S})_2(\text{H}_2\text{O})_2]$ , were synthesised using thiourea as source for the sulfide ion. The morphology of complex sulfides was studied by Transmission Electron Microscopy (TEM). The thermal behavior was studied by DTA–TG technique.

### INTRODUCTION

It was shown that different reagents (like  $\text{H}_2\text{S}$ ,  $\text{S}_8$ ,  $\text{S}_x^{2-}$ ,  $\text{SCN}^-$ ,  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{RNSNR}$  or  $\text{RSH}$ ,  $\text{H}_2\text{NCSNH}_2$ , etc.) can be used to generate sulfide ion as well as sulfide ligands. The complex compounds with ligands having sulfur as donor atom and/or sulfide ions as ligands are interesting for many reasons (i.e., biological importance, unusual structural chemistry, possible use as catalysts or as metal sulfide precursor).<sup>1-3</sup> *p*-Diaminobenzene can act as bridging ligand, in polynuclear complexes, or as monodentate ligand.<sup>4</sup>

In this work we report the synthesis and characterisation of heterometallic complex sulfides of cadmium with *p* - diaminobenzene, using thiourea to generate sulfide ion and the study of complex sulfides as precursors for mixed metal sulfides.

### RESULTS AND DISCUSSION

The system  $\text{Cd}(\text{CH}_3\text{COO})_2 : \text{FeSO}_4 : \text{thiourea} : p\text{-diaminobenzene}$  generated two complex sulfides,  $[\text{CdFe}_2(\text{pdab})_2(\text{S})_3(\text{H}_2\text{O})_6] \cdot \text{H}_2\text{O}$  and  $[\text{CdFe}(\text{pdab})_2(\text{S})_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ , which were characterised by elemental analysis, IR spectra, electronic spectra, thermal analysis and TEM.

From the examination of IR data (Table 1) the following conclusions result:<sup>5-7</sup>

The spectra of both complexes contain bands assigned to *p*-diaminobenzene and no bands assigned to thiourea are found;

The very strong band at  $1105 \text{ cm}^{-1}$  can be assigned to skeleton vibrations of the coordinated aromatic amine;

\* Corresponding author: E-mail: [adumbrava@univ-ovidius.ro](mailto:adumbrava@univ-ovidius.ro)

\*\* Deceased in April 2005

The shift of  $\nu_s(\text{NH}_2)$  and  $\nu_a(\text{NH}_2)$  bands to higher energies suggests that *p*-diaminobenzene is coordinated through nitrogen atoms. The same coordination mode is proved by the shift of  $\nu(\text{CN})$  and  $\delta(\text{NH}_2)$  bands to lower energies;

The presence of several bands in the range of  $\nu(\text{NH}_2)$  vibration in the spectra of both complexes can be correlated with the simultaneous existence of both coordinated and free amino groups;<sup>7</sup>

The bands assigned to  $\rho_w(\text{OH})$  and  $\nu(\text{OH})$  prove the presence of  $\text{H}_2\text{O}$  in both complexes.

Table 1

IR frequencies of *p*-diaminobenzene (pdab), thiourea,  $[\text{CdFe}_2(\text{pdab})_2(\text{S})_3(\text{H}_2\text{O})_6] \cdot \text{H}_2\text{O}$  (1) and  $[\text{CdFe}(\text{pdab})_2(\text{S})_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$  (2) ( $\text{cm}^{-1}$ ).

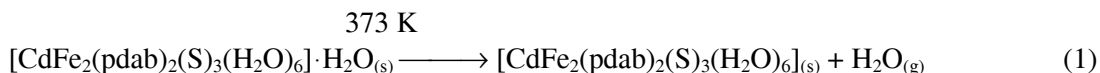
pdab	tu	1	2	Assignments
-	415 m	-	-	$\delta(\text{NCS})$
-	488 m	-	-	$\delta(\text{NCN})$
514 vs	-	516 w	-	$\nu$ ring
-	-	530 w	536 w	$\nu(\text{Fe-S})$
-	-	588 m	581 m	$\rho_w(\text{H}_2\text{O})$
-	730 m	-	-	$\nu(\text{C=S}) + \nu(\text{NCN})$
719 s	-	750 w	749 w	$\gamma(\text{NH}_2)$
829 s	-	846 m	846 m	$\gamma(\text{CH})$
-	1083 m	-	-	$\nu(\text{NCN}) + \gamma(\text{NH}_2) + \nu(\text{C=S})$
-	-	1096 vs	1105 vs	skeleton vibrations
1261 s	-	1225 w	1224 w	$\nu(\text{C-N})$
-	1380 m	-	-	$\nu(\text{NCN}) + \nu(\text{C=S})$
-	1414 s	-	-	$\gamma_r(\text{NH}_2) + \nu(\text{NCN}) + \nu(\text{C=S})$
-	1472 m	-	-	$\nu(\text{NCN})$
1516 vs	-	1519 s	1520 s	$\nu(\text{C=C})$
1628 m	1620 m	1588 m	1583 m	$\delta(\text{NH}_2)$
3200 m	3176 m	3230 m	3225 w	$\nu_s(\text{NH}_2)$
		3256 m	3272 m	
3300 m	3277 m	3296 m	3295 w	$\nu_a(\text{NH}_2)$
3375 m	3382 m	3325 m	3332 m	
-	-	3430 m, broad	3450 m, broad	$\nu(\text{OH})$

vs = very strong, s = strong, m=medium, w = weak

Data on stereochemistry of iron in  $[\text{CdFe}(\text{pdab})_2(\text{S})_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$  have been obtained from the electronic spectrum, in which a band characteristic to  $\text{Fe}(\text{II})$  ion, high spin, in an octahedral configuration ( ${}^5\text{T}_2 \rightarrow {}^5\text{E}$  at  $8772 \text{ cm}^{-1}$ ) was found. For  $[\text{CdFe}_2(\text{pdab})_2(\text{S})_3(\text{H}_2\text{O})_6] \cdot \text{H}_2\text{O}$  spectral data are insufficient for stereochemical information. A charge transfer, probably from metal ion to ligand (MLCT above  $26315 \text{ cm}^{-1}$ ) is found in spectra of both complexes and bands assigned to ligand *p*-diaminobenzene are also observed.<sup>8</sup>

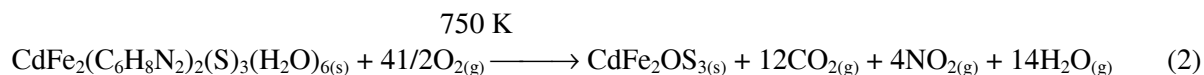
Thermal decomposition of complex  $[\text{CdFe}_2(\text{pdab})_2(\text{S})_3(\text{H}_2\text{O})_6] \cdot \text{H}_2\text{O}$  in the temperature range 293 - 1273 K, at a heating rate of  $10 \text{ K} \cdot \text{min}^{-1}$ , occurs in three steps (Fig. 1):

a) The first step, in the temperature range of 363 - 403 K, is endothermic and is due to elimination of uncoordinated water molecule:



$\Delta m_{\text{found}} = 3.14\%$ ;  $\Delta m_{\text{calc.}} = 2.79\%$ . The temperature written above the arrow corresponds to the maximum decomposition rate as shown by the DTG curve;

b) The second step, in the temperature range of 403 - 848 K, exothermic, is not uniform and consists in elimination of coordinated water molecules, oxidation of  $\text{Fe}(\text{II})$  to  $\text{Fe}(\text{III})$  and combustion of *p*-diaminobenzene:



$\Delta m_{\text{found}} = 46.64\%$ ,  $\Delta m_{\text{calc.}} = 45.03\%$ . The obtained oxosulfide was isolated and characterised;

c) The third step, in the temperature range of 1123 - 1223 K, consists in the decomposition of oxosulfide to metallic cadmium and iron(III) oxide:

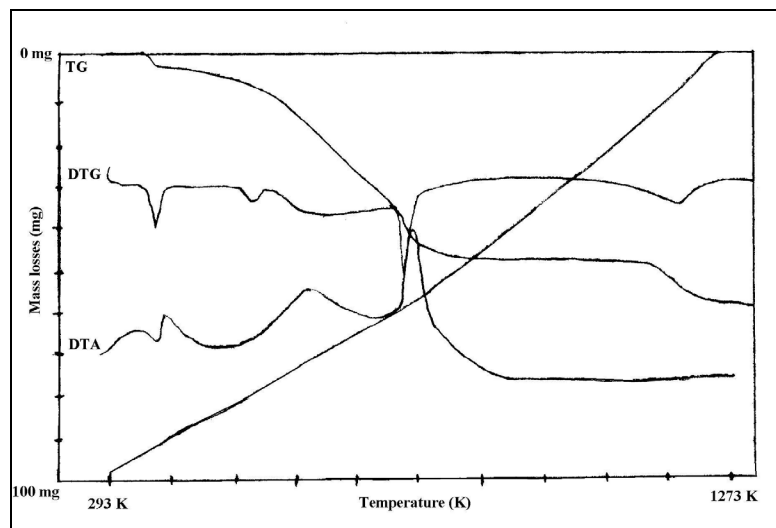
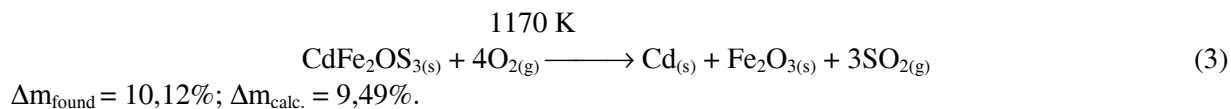


Fig. 1 – DTA - TG curves for  $[\text{CdFe}_2(\text{pdab})_2(\text{S})_3(\text{H}_2\text{O})_6] \cdot \text{H}_2\text{O}$ .

The morphology and size of particles is illustrated by TEM imaging. 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.<sup>9</sup>

Figure 2 shows the bright field TEM micrographs of  $[\text{CdFe}_2(\text{pdab})_2(\text{S})_3(\text{H}_2\text{O})_6] \cdot \text{H}_2\text{O}$ . The figure indicates that most particles are square thin flakes. The thin plates seem to be obtained from thin nanorods.

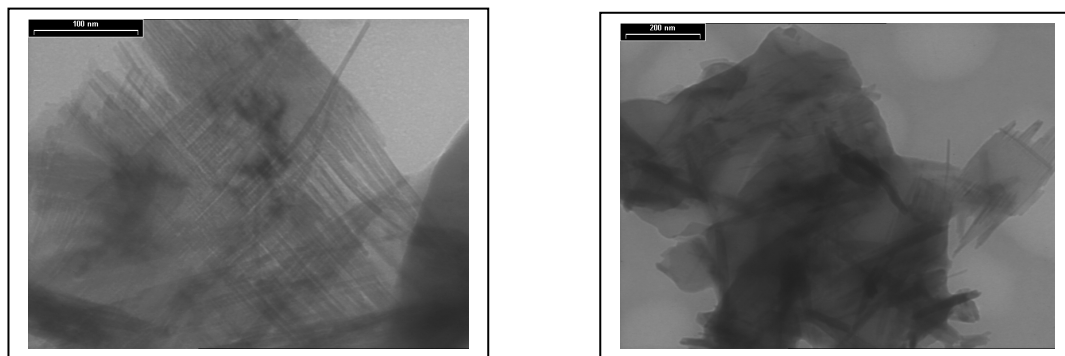


Fig. 2 – TEM images of  $[\text{CdFe}_2(\text{pdab})_2(\text{S})_3(\text{H}_2\text{O})_6] \cdot \text{H}_2\text{O}$ .

The morphology of  $[\text{CdFe}(\text{pdab})_2(\text{S})_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$  particles is shown in Figure 3. Most are nanorods with a medium length of approximately 120 nm and a medium width of approximately 10 nm.

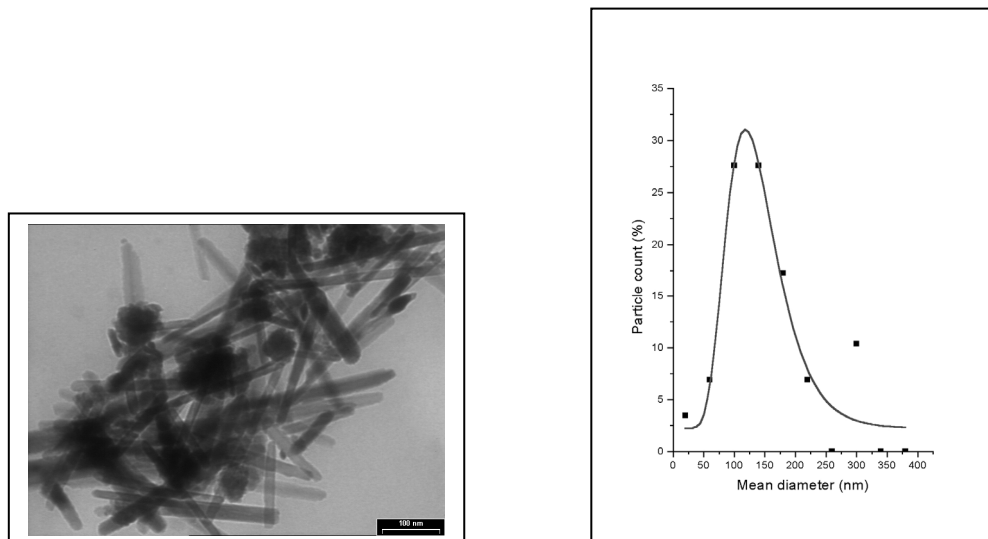


Fig. 3 – TEM image of [CdFe(pdab)<sub>2</sub>(S)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>].4H<sub>2</sub>O (a); mean particle size and particle distribution of [CdFe(pdab)<sub>2</sub>(S)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>].4H<sub>2</sub>O (b).

Controlled thermal decomposition of [CdFe<sub>2</sub>(pdab)<sub>2</sub>(S)<sub>3</sub>(H<sub>2</sub>O)<sub>6</sub>].H<sub>2</sub>O produced CdFe<sub>2</sub>OS<sub>3</sub>. The morphology of CdFe<sub>2</sub>OS<sub>3</sub> was studied by TEM (Fig. 4). The figure indicates that most particles are fine spheres and the size distribution of particles is narrowly dispersed. Mean diameter of particles is evaluated by arithmetic mean of diameters measured at different angles (0, 15, 30, ...180 deg), assuming lognormal distribution of nanoparticles. On the basis of medium diameter of 18.05 nm, CdFe<sub>2</sub>OS<sub>3</sub> prepared by thermal decomposition of complex sulfide, can be included in the nanomaterials category.

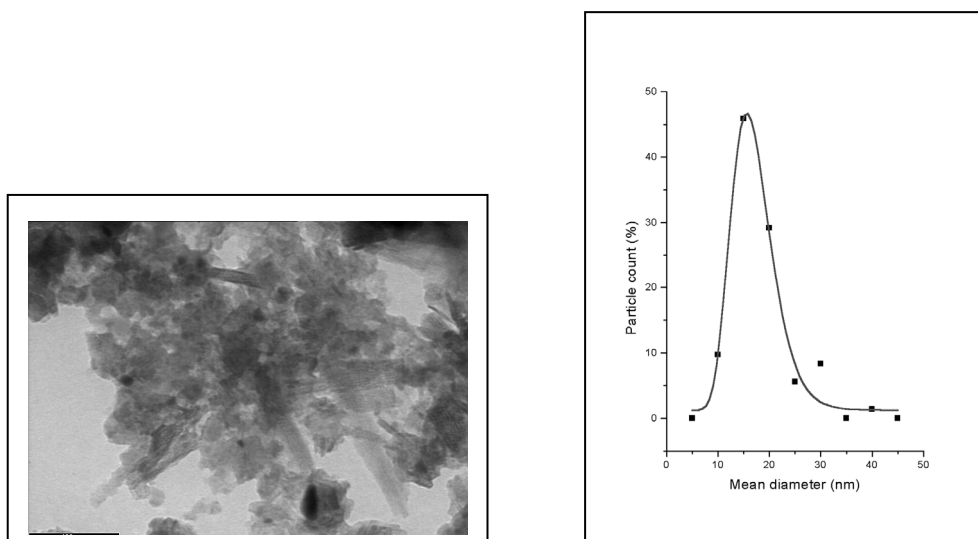


Fig. 4 – TEM image of CdFe<sub>2</sub>OS<sub>3</sub> (a); mean particle size and particle distribution of CdFe<sub>2</sub>OS<sub>3</sub> (b).

## EXPERIMENTAL

All chemicals were of reagent grade quality. Characterisation was made by elemental chemical and spectroscopic methods.

### Synthesis of [CdFe<sub>2</sub>(pdab)<sub>2</sub>(S)<sub>3</sub>(H<sub>2</sub>O)<sub>6</sub>].H<sub>2</sub>O

In a solution of 5 mmol (1.33 g) Cd(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O in 100 mL water were added 10 mmol (2.78 g) FeSO<sub>4</sub>·7H<sub>2</sub>O and 15 mmol (1.62 g) *p*-diaminobenzene. In the resulting solution, stirred at room temperature for 10 min, were added 30 mmol (2.28 g) of thiourea. After 24 hours, the resulting brown precipitate was collected by vacuum filtration, washed with small amounts of hot water

and dried. Elemental analysis (%): Calc. for  $C_{12}H_{30}O_7N_4S_3CdFe_2$ : Cd, 17.39; Fe, 17.39; S, 8.70; N, 8.69. Found: Cd, 18.12; Fe, 17.78; S, 8.88; N, 9.33.

#### Synthesis of $[CdFe(pdab)_2(S)_2(H_2O)_2] \cdot 4H_2O$

In a solution of 5 mmol (1.33 g)  $Cd(CH_3COO)_2 \cdot 2H_2O$  in 100 mL water were added 10 mmol (2.78 g)  $FeSO_4 \cdot 7H_2O$  and 15 mmol (1.62 g) *p*-diaminobenzene. In the resulting solution, stirred at room temperature for 10 min, were added 30 mmol (2.28 g) of thiourea. The mixture was heated for two hours. The resulting brown precipitate was collected by vacuum filtration, washed with small amounts of hot water and dried. Elemental analysis (%): Calc. for  $C_{12}H_{28}O_6N_4S_2CdFe$ : Cd, 20.14; Fe, 10.07; S, 11.51; N, 10.07. Found: Cd, 20.48; Fe, 10.46; S, 10.78; N, 9.76.

Infrared spectra were recorded with a BRUCKER VECTOR 22 FTIR spectrometer in KBr pellets in the 4000 - 400  $cm^{-1}$  range.

Electronic spectra were recorded with a VSU2-P spectrometer in the 380 - 1200 nm range, using MgO as standard.

Thermal analysis was performed with a Q-1500 Paulik–Paulik–Erdely derivatograph, in a static air atmosphere, with  $\alpha$  -  $Al_2O_3$  as the inert reference compound, at a heating rate of 10 K/min, in the range 293 - 1273 K. The sample mass was between 90 - 100 mg.

The TEM's were made with the Philips CM 120 transmission electron microscope, operated at 100 kV, with 2 Å resolution.

## CONCLUSIONS

Using thiourea as a source of sulfide ion, two heterometallic complex sulfides of cadmium and iron with *p*-diaminobenzene as ligand were synthesised.

Thermal decomposition of  $[CdFe_2(pdab)_2(S)_3(H_2O)_6] \cdot H_2O$  gave  $CdFe_2OS_3$  nanoparticles.

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