J Therm Anal Calorim (2011) 106:601–606
DOI 10.1007/s10973-011-1341-z

# Thermal decomposition study of bismuth (III) trichloride complex with 1,10-phenanthroline as the ligand

**José Geraldo de P. Espínola · Evandro P. S. Martins ·**
**Franklin P. Aguiar · Haryane R. M. Silva · M. G. Fonseca ·**
**L. N. H. Arakaki · Ercules E. S. Teotônio**

CBRATEC7 Conference Special Issue

**Abstract** The complex $BiCl_3 \cdot L$ (L = 1,10-phenanthroline) was synthesized and characterized by elemental analysis and infrared spectroscopy (IR). Infrared spectroscopy data suggested that the nitrogen atom of the aromatic ring is bonded to the bismuth atom. The kinetic study of thermal degradation was determined by non-isothermal thermogravimetry. Two methods based on integral equation of Coats-Redfern, were necessary for determining the kinetic trip: the fitting method, known as the checking model and an iso-conversional method. The latter gives the activation energy for each degree of conversion and the first, the kinetic model gives activation energy and the pre-exponential factor for thermal decomposition processes that occur through a single simple mechanism. The kinetic parameters, $E_a$ and log $A$ for the heating rates of 5, 10, and 15 min $K^{-1}$, were determined considering the decomposition model denoted by F0/R1 in the range of degree of conversion between 0.065 and 0.71.

**Keywords** Bismuth complex · Decomposition kinetic · Phenanthroline

## Introduction

The element bismuth, in its compounds, is found in various oxidation states, the most common being +3 and +5, as in bismuth halides [1] and bismuth derivatives with transition metals [2–4]. These two classes of compounds of bismuth have been extensively researched. Another aspect is the fact that this element can coordinate with up to ten atoms ligands, forming compounds that exhibit a variety of structural forms. Complexes of bismuth (III) have been applied in various fields of human activity, and medicine [5], catalysis [6], the chemistry of solids [7], among others. Some medical studies explored the effects of bismuth compounds against malaria [8, 9], others used bismuth compounds as precursors for to synthesize $Bi_2O_3$ films by chemical vapor deposition (CVD), including bismuth halides and bismuth triphenyl, $Bi(Ph)_3$ [10], but, the halides are known to be toxic and corrosive and the triphenyl, in spite of safety and offers remarkable advantages in terms of thermal stability and clean sublimation a difficult more synthesis, it is more expensive. In this study, a complex $BiCl_3 \cdot L$ where L is 1,10-phenanthroline was obtained and characterized. Thus, considering that the thermogravimetry experiments carried out in this the laboratory shows that the $BiCl_3 \cdot$phen complex sublime, such complex might to replace precursor as $BiCl_3$ and $Bi(Ph)_3$ in the synthesis of $Bi_2O_3$ films by chemical vapors deposition (CVD). In this case, it was studied the behavior of this complex in relation to the thermal stability and their kinetics of thermal degradation. Thus, thermal analysis techniques as non-isothermal thermogravimetry (TG) and differential thermal analysis (DTA) were used for the obtaining process data from the complex thermal degradation.

## Theoretical foundations

In determining the kinetic trip, activation energy, the pre-exponential factor and the possible decomposition mechanism of the complex, two methods of analysis of

---

J. G. de P. Espínola (✉) · E. P. S. Martins ·
F. P. Aguiar · H. R. M. Silva · M. G. Fonseca ·
L. N. H. Arakaki · E. E. S. Teotônio
Departamento de Química, Centro de Ciências Exatas e da Natureza, Universidade Federal da Paraíba,
João Pessoa, PB, Brazil
e-mail: jgespinola@bol.com.br

thermo-gravimetric curves were used, which are based on the Coats–Redfern equation: model fixing [11], and iso-conversional methods. In general, the rate law of a decomposition reaction in the solid state is expressed as $d\alpha/dt = A \exp(-E_a/RT) f(\alpha)$ where $\alpha$ is the degree of conversion, t is time, A is the pre-exponential factor, $f(\alpha)$ is a function of $\alpha$, and $E_a$ is the activation energy [12].

For decomposition reactions, the most widely used methods for kinetic studies of solid state are isothermic, semi-isothermic, isothermic, and non isothermic, mostly non isothermic. However, the most widely used method is non isothermic, where the degree of conversion is obtained depending on the temperature. That is, for each temperature there is only one value for the degree of conversion. In this case, the data relative to the degree of conversion can be obtained for linear or nonlinear heating rates.

The ICTAC Kinetic Analysis project [13] recommends that $E_a$ and A for decomposition under non isothermal conditions is calculated primarily by the iso-conversional method; Model-free, which has the advantage of not requiring a specific kinetic model and, thus, denying any dependence on this choice. Iso-conversional methods are used to calculate a rate constant instantaneous reaction rate constant as a function of conversion degree, and then determines the activation energy and frequency factor of an Arrhenius plot, in an extension of constant reaction. In this case, two or more experiments at different heating rates are necessary. According to the literature [13–15] the importance of Model-free analysis lies in its function as a prerequisite for a non-linear regression. In addition, this model also allows distinguishing the various characteristic stages of a process that often can only be detected from the dependence of activation energy in function of the degree of conversion of the reaction.

## Materials and methods

Purification of reagents and solvents used in this study was performed according to the methods cited in the literature [16]. Phen was recrystallized from a supersaturated solution of ligand in acetone. Bismuth trichloride ($BiCl_3$) was purified by sublimation through the following procedure: the impure compound was placed in a round bottom flask of 250 mL and subjected to heating under vacuum at 413 K. The flask was placed horizontally so that the compound would sublime in its upper wall, and a solid with high purity could be obtained.

The complex of bismuth trichloride with phen was prepared using a 100 mL volumetric flask with side entrances for the introduction of nitrogen gas and the addition of solutions. With the aid of an addition funnel, the solution of ligand and 1.03 g of solid was transferred slowly into the flask containing the solution with about 1.9 g of $BiCl_3$ salt. This reaction mixture was kept for 12 h under magnetic stirring. The solid formed, i.e., the complex of bismuth trichloride with phen was filtered and washed with acetone to remove any impurities, and then after dried in a vacuum line was placed in a desiccator.

## Methods of analysis

Infrared spectra in the range 4,000–400 $cm^{-1}$ were obtained at room temperature and in KBr pellets with a Shimadzu spectrophotometer, model Bomen MB-102. Carbon, nitrogen, and hydrogen were determined using a PerkinElmer trace analyzer, model PE-2400. The bismuth content was estimated by atomic absorption after the dissolution of the HNO3 complex, using a GBC, model 908 AA device for spectroscopy. The chlorine content was calculated using the Volhard method after resolution of the $HNO_3$ complex as well. Thermal decomposition was performed using a Shimadzu thermo-balance, model TG-50. Thermo-gravimetric curves were obtained by non-isothermic technique, where masses of 5.0 ± 0.5 mg samples were heated in a nitrogen flow of 50 $cm^3\ s^{-1}$ and linear heating rates of 5, 10, and 15 K $min^{-1}$.

For kinetic analysis of TG curves two methods were used: the iso-conversional method to determine the activation energy for each experimental point of conversion between 0.01 and 0.95 and the integral method of Coats-Redfern for simple linear regression [9]. The latter method was used for a topo-chemistry equation study (a selection of 18 equations: the chemical reaction at the interface, nucleation, and diffusion [17] for the region where the authors detected constancy in the kinetic parameter values for the curve obtained by iso-conversional method for the set of experimental data.

The Coats-Redfern equation used to calculate the kinetic parameters can be expressed as:

$$\ln\left(\frac{g(\alpha)}{T^2}\right) = \ln\left(\frac{AR}{\beta E_a}\right)\left(\frac{1 - 2RT_{exp}}{E_a}\right) + \frac{E_a}{RT} \qquad (1)$$

where$T_{exp}$ = the average temperature experimental, $E_a$ = activation energy, $A$ = pre-exponential factor, $\beta$ = heating rate, $R$ = universal gas constant, and $g(\alpha)$ = a function that describes the mechanism of degradation of the condensed phase.

## Results and discussion

The data of infrared spectroscopy and elemental analysis of the complex are shown in Table 1. The results of elemental analysis of solid complex are in complete agreement with

**Table 1** Elemental data, phase change temperature pct (K) and IR absorption bands ($cm^{-1}$) for complex of bismuth trichloride with 1,10-phenanthroline

| Compound | $\delta$ CH | $\nu$ ring | $\nu$ CC/ $\nu$CN | $\nu$CH | $\nu$CH/$\nu$OH | %C | %H | %N | pct/ K |
|---|---|---|---|---|---|---|---|---|---|
| Phen | 728 | 1417 | 1510 | 3045 | – | | | | |
| $BiCl_3$·L | 728 | 417 | 1505 | 3057 | 3057 | 29.05 | 2.01 | 5.65 | |
| *$BiCl_3$·L | – | | | | | 29.65 | 2.05 | 5.88 | 592 |

$\upsilon$ stretching; $\delta$ deformation; * theoretical

the general formula $BiCl_3$·L (L = phen). The infrared spectra absorption bands for both ligand and complex were based on the literature [18–20] and they are listed in Table 1. It was observed that some bands of the ligand in the complexes were shifted in comparison with the absorption of free ligand. However, the main vibrational bands in the spectrum of the complex showed the same characteristics as those in free ligand, suggesting that the vibration modes were unchanged after coordination with bismuth trichloride.

## Thermogravimetry and differential thermal analysis

TG curves of the complex $BiCl_3$·phen were obtained at heating rates of 5, 10, and 15 K $min^{-1}$ in the temperature range 471–900 K. Figure 1 depicts the profile curve obtained at speeds of 5, 10, 15, and 20 K $min^{-1}$. Table 2 lists the data on mass losses occurring in the stages of degradation of the complex.

The profiles of the TG curves showed the same thermal behavior and that the mass loss of the complex occurs in three stages: the first in the range of 477–731 K (mass loss 70%), attributed to sublimation and vaporization of the complex, the second in the range of 731–909 K (mass loss 13%), attributed to degradation of the salt $BiCl_3$, and third, above 909–1173 K related to the degradation of residues. Also, the increase in heating rate causes an increase in temperature for the same degree of conversion. DTA curves obtained at speeds of 10 and 20 K $min^{-1}$ are shown in Fig. 2. This curve shows four endothermic transitions: the first two, being one large and one acute, are in the range of 559–602 K, and were associated with the sublimation and melting of the complex, the third in the region of 709 K, corresponds to $BiCl_3$ fusion, and the fourth, residue elimination.

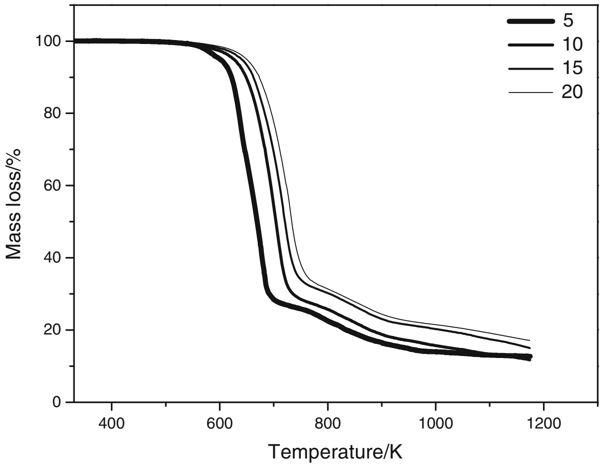

**Fig. 1** TG curves of $BiCl_3$·Phen at heating rates of 5, 10, 15, and 20 K $min^{-1}$

### Kinetic analysis

In this study kinetic data were analyzed only for the first stage of degradation of the complex in each linear velocity of heating. These TG data were processed according to the "Model-free" method, without considering the topo-chemistry equations of the kinetics for solid state. A program based on Eq. 2 below was used to determine the activation energy of degradation of the complex in the range of $\alpha$ between 0.01 and 0.98.

$$E_a = 2\ln\left(\frac{T_i}{T_j}\right) - \ln\left(\frac{\beta_i}{\beta_j}\right)\left(\frac{T_i.T_j}{T_j - T_i}\right)R \tag{2}$$

where $T_i$ and $T_j$ are the temperatures for the same degree of conversion corresponding to linear velocities of heating and $\beta_i$ $\beta_j$. It allows calculation of the activation energy for each experimental point of fractional conversion (in the range $0.01 < \alpha < 0.98$, combination of multiple curves). Equation 2 was obtained from the integral equation of Coats–Redfern [11] as follows: applying logarithm on both sides of Eq. 1 the values for two different linear heating rates for the same value of $\alpha$, and considering also that the kinetic parameters, activation energy and pre-exponential factor, are constants, gives:

$$\ln(g(\alpha)) = \ln\left(\frac{AR}{E_a\beta_1}\right) + \ln\left(\frac{1 - 2RT_{exp}}{E_a}\right) - \frac{E_a}{RT_1} \tag{3}$$

$$\ln(g(\alpha)) = \ln\left(\frac{AR}{E_a\beta_2}\right) + \ln\left(\frac{1 - 2RT_{exp}}{E_a}\right) - \frac{E_a}{RT_2} \tag{4}$$

If you consider that the ln $(1\text{-}2RT_{exp}/E_a)$ in both equations will be approximately the same order for both heating rates, Eq. 2 becomes

$$\ln\left(\frac{AR}{E_a\beta_1}\right) - \frac{E_a}{RT_1} = \ln\left(\frac{AR}{E_a\beta_2}\right) - \frac{E_a}{RT_2} \tag{5}$$

this equation, rearranged, gives the reaction (2).

The activation energy for the degradation of the complex was taken as the average activation energy for the six possible combinations of $T_i$, $T_j$, and $\beta_i$, $\beta_j$ for the three

**Table 2** Data on mass losses occurring in the stages of degradation of the $BiCl_3$·Phen complex

| Stages | $\Delta T_{experimental}$/K | Mass/% | Attributions |
|---|---|---|---|
| 1 | 731–477 = 254 | 70 | Sublimation and vaporization of the complex |
| 2 | 909–731 = 178 | 13 | Degradation of the salt $BiCl_3$ |
| 3 | 1173–909 = 264 | 17 | Degradation of residues |
| Total | | 100 | |

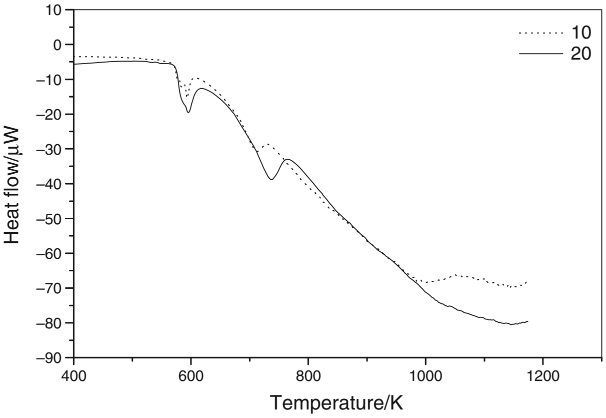

**Fig. 2** DTA curves of $BiCl_3$·Phen at heating rates 10 and 20 K $min^{-1}$

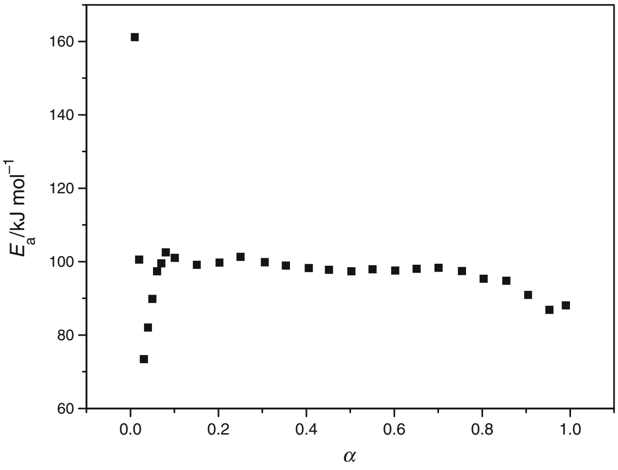

**Fig. 3** $E_a$ of $BiCl_3$·Phen at different conversion degrees

**Table 3** Fitted kinetic parameters at non-isothermal decomposition condition using the Coats–Redfern method

| Compound | Model | $A/s^{-1}$ | $E_a$/kJ $mol^{-1}$ | $R^2$ |
|---|---|---|---|---|
| $BiCl_3$·phen | P1 | $1.29 \times 10^{12}$ | 156.414187 | 0.9990 |
| | P2 | $1.84 \times 10^{4}$ | 44.827479 | 0.9980 |
| | P3 | $5.26 \times 10^{2}$ | 26.116642 | 0.9980 |
| | P4 | $7.50 \times 10^{1}$ | 16.760802 | 0.9980 |
| | A2 | $1.57 \times 10^{5}$ | 57.044398 | 0.9970 |
| | A3 | $2.43 \times 10^{3}$ | 34.224307 | 0.9940 |
| | A4 | $2.58 \times 10^{2}$ | 22.84134 | 0.9930 |
| | F0/R1 | $3.97 \times 10^{8}$ | 100.970833 | 0.9990 |
| | R2 | $1.22 \times 10^{9}$ | 112.555803 | 0.9980 |
| | R3 | $1.26 \times 10^{9}$ | 116.684999 | 0.9980 |
| | D1 | $5.20 \times 10^{16}$ | 213.253384 | 0.9990 |
| | D2 | $2.93 \times 10^{17}$ | 227.967635 | 0.9990 |
| | D3 | $9.76 \times 10^{17}$ | 244.675873 | 0.9980 |
| | D4 | $1.61 \times 10^{17}$ | 233.512067 | 0.9990 |
| | F1 | $2.03 \times 10^{10}$ | 125.354671 | 0.9980 |
| | F2 | $2.33 \times 10^{12}$ | 147.667357 | 0.9830 |
| | F3 | $1.05 \times 10^{15}$ | 177.11828 | 0.9650 |

heating rates: 5, 10, and 15 K $min^{-1}$. The curve in Fig. 3 shows the activation energy versus conversion degree for the thermal degradation process of $BiCl_3$·phen. In this figure, it appears that the activation energy varied as a function of α as follows: increases in the range from 0.03 to 0.065; remains constant from 0.065 to 0.71 and decreases in the range from 0.71 to 0.98.

The same set of experimental data was also used to find the topo-chemistry equation (a selection of 18 equations: the interface chemical reaction, nucleation and diffusion [17]). The choice of the topo-chemistry equation was made using the Coats–Redfern equation, using the linear fitting method for the degrees of conversion where the Model-free method detected a constancy of values of activation energy with the degree of conversion.

According to Khawam and Flanagan [21] if the calculations, based on the method of adjusting the equation of Coats–Redfern, provide two or more kinetic equations with the same correlation coefficient, but with noticeable differences in kinetic parameters it is reasonable, to select the equation with values of kinetic parameters closest to the result obtained by the iso-conversional method. For the complex, using the linear fitting method, several kinetic trips were calculated from the Coats–Redfern equation, as shown in Table 3. The results clearly show that the correlation coefficients (*r*) for different models used are indistinguishable (for example, models D1, D2, D4, and F0/R1). On the other hand, the plot of the degradation (Fig. 4) using the iso-conversional model shows that the F0/R1 model can be selected as model most appropriate for the kinetic study of the complex because $E_a$ for F0/R1,

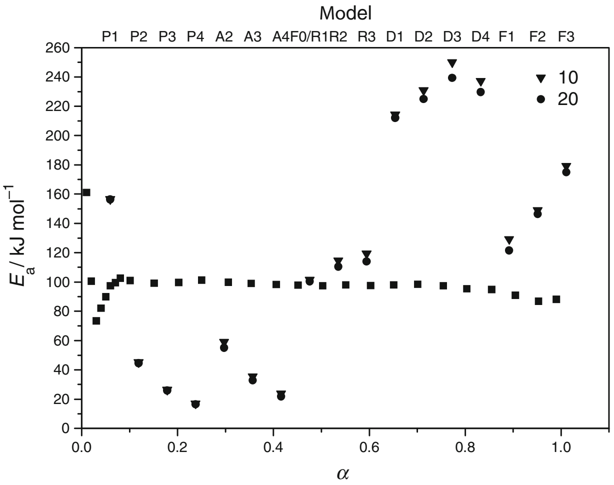

**Fig. 4** Iso-conversional model plot of activation energies for non-isothermal degradation of the $BiCl_3$·Phen complex calculated by Coats–Redfern's modelistic method (*filled inverted triangle* and *filled circle*) and iso-conversional method based in Eq. 2 (*filled square*)

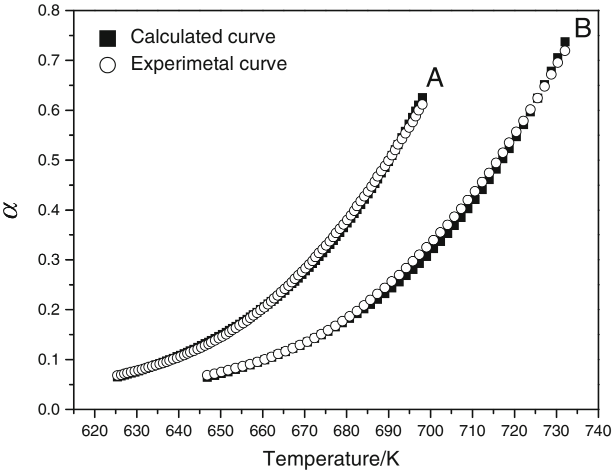

**Fig. 5** Reconstructed R–T plots for non-isothermal degradation of the $BiCl_3$·Phen complex for two heating rates ($A = 10$ and $B = 20$ K/min): experimental (*filled square*) and reconstructed (*open circle*) curves

calculated by the Coats–Redfern method, is almost the same as that calculated by equation two iso-conversional method (~99 kJ/mol, Table 3).

Figure 5 shows the plot of α-T for the reconstruction of non-isothermal decomposition at heating rates of 10 and 20 K min$^{-1}$, where good correlations between experimental and reconstructed data were observed. However, for the heating rates of 5 and 15 K min$^{-1}$, the correlation between the reconstructed and experimental curves were not good, which may be because the thermogravimetric balance was not well controlled during the process of decomposition of the samples at these speeds of heating or due the curves were constructed from the average values of $E_a$ and $A$, and they were obtained by an adjustment method for the Coats–Redfern equation. The standard deviations calculated between the values of α, experimental and calculated, for the heating rates in 10 and 20 K min$^{-1}$ were around 0.0085 for the range 0.065–0.71.

## Conclusions

The $BiCl_3$·phen complex was thermally stable up to temperatures around 468 K. The profiles of the TG curves obtained at three heating rates were very similar. The kinetic model with best fit the TG data was F0/R1 for the region of degree of conversion found in the range from 0.065 to 0.71. In regions below 0.065 and above 0.71, $E_a$ decreased, indicating more than one process contributing to the degradation of the complex. The reconstruction of α-T curve from the kinetic trip ($E_a$, $A$, and F0/R1) showed close agreement with the experimental α-T curve for a range of degree of conversion from 0.065 to 0.71 in the heating rate of 10 K min$^{-1}$.

## References

1. Fisher GA, Norman NC. Synthetic and structural studies on organomolybdenum–bismuth halide complexes. Zeitschrift für anorganische und allgemeine Chemie. 1994;620:457–66.
2. Luan SR, Zhu YH, Jia YQ, Cao Q. Characterization and thermal analysis of thiourea and bismuth trichloride complex. J Therm Anal Calorim. 2010;99:523–30.
3. Norman NC, Meldola ML. Organotransition metal-complexes incorporating bismuth. Chem Soc Rev. 1988;17:269–81.
4. Clegg W, Compton NA, Herrington RJ, Fisher GA, Hockless DCR, Norman NC, Williams NAL, Stratford SE, Nichols SJ, Jarrett PS, Orpen AG. Structural studies on organotransition-metal bismuth complexes. J Chem Soc Dalton Trans 1992; 193–201.
5. Solanki JS, Tripathi UN, Bhardwaj A, Thapak TR. Synthesis, spectral sudy and antimicrobial activity of bismuth(III) 3(2′-hydroxyphenyl)-5-(4-substituted phenyl) pyrazolinates. J Coord Chem. 2008;61:4025–32.
6. Wang YJ, Xu L, Wang XU. Synthesis and crystal structure of bis(hsal)(3)(1,10-phenanthroline) (Hsal = O2CC6H4–2-OH). Chinese J Struct Chem. 2008;27:297–300.
7. Tershansy MA, Goforth AM, Peterson L, Burns MC, Smith MD, zur Loye HC. Syntheses and crystal structures of new chain-containing iodometallate compounds: [H1, 10-phen](H2O)(1.41)[AgI2], [H1, 10-phen](H2O)(1.42)[CUI2]; [Co(tPY)(2)][Bi2I8], [Fe(tPY)(2)] [Bi2I8]; [Co(1, 10-phen)(3)][Pb3I8]center dot H2O, and [Fe(1, 10-phen)(3)][Pb3I8]center dot 0.5(H2O). Solid State Sci. 2007;9:895–906.
8. Yang N, Sun H. Biocoordination chemistry of bismuth: Recent advances. Coord Chem Rev. 2007;251:2354–66.
9. Gabbiani C, Messori L, Cinellu MA, Casini A, Mura P, Sannella AR, Severini C, Majori G, Bilia AR, Vincieri FF. Outstanding plasmodicidal properties within a small panel of metallic

compounds: hints for the development of new metal-based antimalarials. J Inorg Biochem. 2009;103:310–2.

10. Bedoya C, Condorelli GG, Anastasi G, Baeri A, Scerra F, Fragala‘ IL. Chem Mater. 2004;16:3176.
11. Coats AW, Redfern JP. Kinetic parameters from thermogravimetric data. Nature. 1964;201:68–9.
12. Brown ME, Dollimore D, Galwey AK. Comprehensive chemical kinetics. 22nd ed. Amsterdam: Elsevier; 1980.
13. Brown ME, Macejewski M, Vyazovkin S, Nomen R, Sempere J, Burnham A, Opfermann L, Strey R, Anderson HL, Kemmler A, Reuleers R, Janssens J, Desseyn HO, Li CR, Tang TB, Roduit B, Malek J, Mitsuhashi T. Computational aspects of kinetic analysis Part A: the ICTAC kinetics project-data, methods and results. Thermochimica Acta. 2000;355:125–43.
14. Logvinenko V, Chingina T, Sokolova N, Semyannikov P. Thermal decomposition of bismuth stearates—study of process kinetics. J Therm Anal Calorim. 2003;74:401–5.
15. Rotaru A, Gosa M. Computational thermal and kinetic analysis. Complete standard procedure to evaluate the kinetic triplet form non-isothermal data. J Therm Anal Calorim. 2009;97:421–6.
16. Basset J, Denney RC, Jeffery GH, Mendham J. Análise inorgânica quantitativa. 4th ed. Rio de Janeiro: Editora Guanabara; 1981.
17. Mamleev V, Bourbigot S. Modulated thermogravimetry in analysis of decomposition kinetics. Chem Eng Sci. 2005;60:747–66.
18. Nakamoto K. Infrared and Raman spectra of inorganic and coordination campounds-applications in coordination, organometallic, and bioinorganic chemistry. 6th ed. New Jersey: John Wiley & Sons; 2009.
19. Vallette MMC, Clavijo RE, Mendizabal F, Zamudio W, Baraona R, Diaz G. Infrared spectrum of the bis-(1, 10-phenanthroline) Cu(I) and Cu(II) perchlorate complexes. Vib Spectrosc. 1996;12:37–44.
20. Reiher M, Brehm G, Schneider S. Assignment of vibrational spectra of 1, 10-phenanthroline by comparison with frequencies and Raman intensities from density functional calculations. J Phys Chem A. 2004;108:734–42.
21. Khawam A, Flanagan DR. Complementary use of model-free and modelistic methods in the analysis of solid-state kinetics. J Phys Chem B. 2005;109:10073–80.