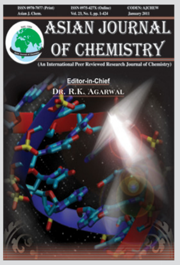
*Asian Journal of Chemistry;* *Vol. 23, No. 6 (2011), 2441-2444*

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in



# Determination of Bismuth by Electrothermal Atomic Absorption Spectrometry using Single Drop Micro Extraction in Real Samples

M. CHAMSAZ*, M.H. ARBAB-ZAVAR, M.M. RIAZI and R. TAKJOO

Department of Chemistry, Faculty of Sciences, Ferdowsi University of Mashhad, Mashhad, Iran

*Corresponding author: E-mail: mchamsaz@gmail.com

(*Received*: 7 May 2010; *Accepted*: 4 February 2011) AJC-9587

A novel and extremely sensitive method for extraction and determination of bismuth in aqueous samples by liquid phase micro extraction (LPME) combined with electrothermal atomic absorption spectrometry using a new ligand is described. In this method $Bi^{3+}$ in pH 6 during 20 min extraction time at 20 ºC is reacted with S-methyl-3-salicylidene dithiocarbazate dissolved in 4 µL of chloroform micro drop. After extraction, the micro drop was retracted and directly transferred into a graphite tube coated by palladium and tungsten with co-injection of tartaric acid as chemical modifier. In this investigation the type of organic solvent, volume of organic solvent, pH, temperature and extraction time were optimized. Using 10 mL sample solution an enrichment factor of 100 was obtained. The detection limit was calculated to be 19 pg $mL^{-1}$ based on $3S_b$ and relative standard deviation for five replicate analysis of 0.5 ng $mL^{-1}$ $Bi^{3+}$ was 4.8 %. The calibration curve was liner in the range of 19 pg $mL^{-1}$ to 2.4 ng $mL^{-1}$ with a sensitivity of 4.0 pg $mL^{-1}$. This method was used for determination of bismuth in tap water, waste water, sea water, soil and reliability of the method was evaluated using two reference materials.

**Key Words: Bismuth, Electrothermal atomic absorption spectrometry, Liquid phase micro extraction, S-Methyl-3-salicylidene dithiocarbazate.**

## INTRODUCTION

Bismuth has been associated with medicine for more than 200 years. This element was first introduced in a pharmacy for treatment of syphilis[1]. Presently, bismuth is used in cosmetics industry for preparation of creams and hair dyes, while some of its colloidal salts (subcitrate and subgallate), due to their antiseptic, astringent and diuretic properties, have found important applications in pharmaceutical preparations and are employed as anti ulcer, antibacterial, anti HIV and radiotherapeutic agents[2]. Although there is little possibility of poisoning from bismuth in industrial applications, there have been several reported cases of nephrotoxic and neurotoxic symptoms from the use of bismuth-containing pharmaceuticals[3-5]. These cases underscore the necessity for sensitive methods to determine bismuth.

Several sensitive methods have been developed for determination of bismuth. These include hydride generation atomic absorption spectrometry[6], electrothermal atomic absorption spectrometry[7], atomic fluorescence spectrometry[8], hydride generation inductively-coupled plasma spectrometry[9], hydride generation atomic fluorescence spectrometry[10,11] electrothermal vaporization inductively coupled plasma mass spectrometry[12], potentiometric stripping analysis[13], anodic stripping voltammetry[14-16], cathodic stripping voltammetry[17] and adsorptive stripping voltammetry[18].

However, direct determination of trace amounts of metals in seawater and biological materials is difficult. This is because of low concentrations of trace amounts of metals and strong interferences from the sample matrix. Preconcentration addresses both of these problems. There are many methods for preconcentration and separation, such as liquid-liquid extraction[19-21] and solid phase extraction[22-28]. Shemirani and Baghdadi reported a cloud point extraction for of bismuth and its determination by electrothermal atomic absorbtion spectrometry[29]. Also Rui Liu and Peng Wu reported atomic fluorescence spectrometry for determination of bismuth[30,31]. In this investigation a new ligand S-methyl-3-salicylidene dithiocarbazate (SMSDC) for microextraction of trace amounts of bismuth is reported.

## EXPERIMENTAL

All reagents were of analytical reagent grade and triply distilled water was used throughout and ligand was prepared with the following method:

**Preparation of S-methyldithiocarbazate:** S-Methyldithiocarbazate was prepared as previously reported[32]. A mixture of KOH (22.8 g, 0.4 mol) and $N_2H_4{\cdot}H_2O$ (20 g, 0.4 mol) in 90 % ethanol (140 mL) was cooled down to 5 ºC. $CS_2$ (30.4 g, 0.4 mol) was added dropwise with stirring. The temperature was kept below 5 ºC all the time. Two layers were formed and the yellow oil was separated and dissolved in 40 % ethanol (60 mL) and the solution was cooled in an ice bath. Methyl iodide (58 g, 0.4 mol) was added slowly with vigorous stirring. The white product was separated by filtration, washed with water and dried in air. The crude product was recrystallized in ethanol; yield: 40 %; m.p. 82 ºC.

**Preparation of S-methyl-3-salicylidene dithiocarbazate (SMSDC):** This compound was prepared as previously reported[33]. S-methyldithiocarbazate (2.4 g, 0.2 mol) was dissolved in 50 mL of hot ethanol. To this solution was added 2.45 g (21.5 mL 0.2 mol) of salicylaldehyde in 50 mL ethanol. The resultant mixture was heated on a steam bath for about 15 min. The precipitated crystals, were filtered off, washed with ethanol, recrystallized in benzene and dried *in vacuo*. Yield: 80 %; m.p. 210 ºC.

A stock 1000 ppm of bismuth solution was prepared by dissolving appropriate amounts of $Bi(NO_3)_3{\cdot}5H_2O$ in 1 % $HNO_3$. 0.4 % (w/v) palladium prepared by dissolving $PdCl_2$ in HCl 2 and 0.4 % (w/v) tungeston prepared by dissolving $Na_2WO_4{\cdot}2H_2O$ in water was coating of graphite tubes and 4.0 % (w/v) tartaric acid prepared in water was used as chemical modifier. 0.2 % (w/v) SMSDC in chloroform was used as acceptor phase. A 10 µL Hamilton syringe was used to suspend the drop of the acceptor phase and to inject it into the graphite furnace atomizer.

A Shimadzu model AA-670 atomic absorption spectrometer with GFA-4B graphite furnace atomizer and $D_2$ lamp for background correction was used.

Bismuth hollow cathode lamp was used as radiation source adjusted at 8 mA. An atomic absorption signal at 223.1 nm line was recorded on a graphic printed PR-4 with peak height and gas stop mode for quantification. The temperature program for the furnace is as follows (Table-1):

TABLE-1
GFA HEATING PROGRAM

| Stage | Furnace temp. (ºC) | Mode | Time (s) | Argon flow rate (L min$^{-1}$) |
|---|---|---|---|---|
| Drying | 150 | Ramp | 15 | 1.5 |
| Ashing | 500 | Step | 15 | 1.5 |
| Atomization | 1900 | Step | 3 | 0 (gas stop) |
| Cleaning up | 2500 | Step | 2 | 1.5 |

**Determination of bismuth *via* preconcentration using single drop micro extraction technique:** 10 mL of Bi(III) solution was adjusted at pH 6 and transferred into a 15 mL vial. The vial was maintained at a temperature of 20 ºC in water-bath and Bi(III) was extracted into a 4 µL chloroform drop containing 0.2 % (w/v) SMSDC on the tip of a Hamilton syringe for 20 min. The solution was stirred (500 rpm) during the extraction (Fig. 1).

After the extraction was completed, the organic phase was directly injected into the graphite tube coated by 60 µL 0.4 % (w/v) palladium and tungeston with co-injection of 20 µL 4 % (w/v) tartaric acid as chemical modifier.

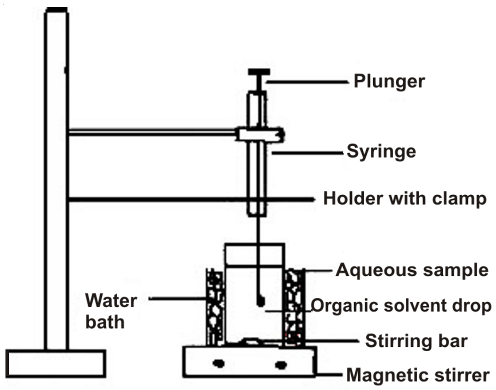


Fig. 1. Schematic setup for single drop micro extraction

## RESULTS AND DISCUSSION

**Optimizing the parameters for extraction:** In order to investigate the effects of different parameters on preconcentration of bismuth by single drop micro extraction, 10 mL solution of 0.5 ng mL$^{-1}$ bismuth was used at all the following stages:

**Solvent:** Different solvents were tested from the volatility and dissolving points of view such as chloroform, dichloromethane, dichloroethane, nitrobenzene and carbon tetrachloride. Chloroform showed the best results for extraction of bismuth complex (Fig. 2).

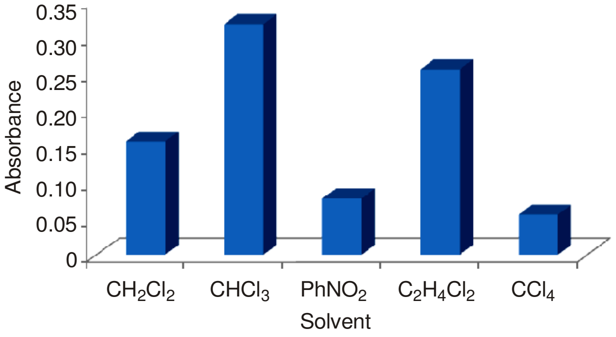


Fig. 2. Effect of solvent

**pH:** The extraction efficiency of the method was tested at different pH. As can be seen from Fig. 3, the best pH was 6. At pH lower than 6, protonation of the nitrogen atoms in ligand molecules occurs and complexion strength of $Bi^{3+}$ is decreased. At pH more than 6, bismuth ions are hydrolyzed and extraction efficiency is decreased.

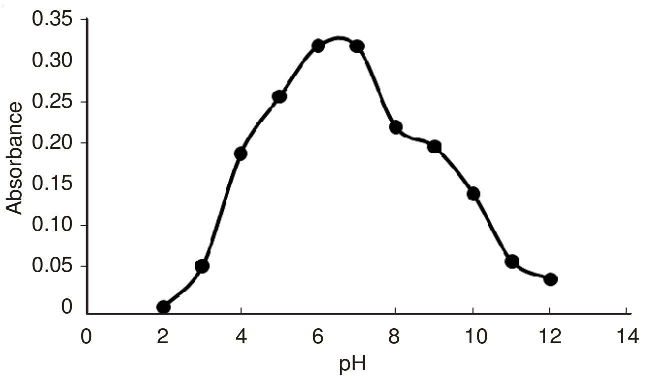


Fig. 3. Effect of pH

**Ligand concentration in organic phase:** The ligand (SMSDC) concentration in organic phase was varied from 0.02-0.4 % (w/v) using 10 mL $Bi^{3+}$ at pH 6. The extraction efficiency was increased with increasing of the ligand concentration up to 0.2 % (w/v) and then leveled off at higher concentrations (Fig. 4). As the results show the optimum concentration of ligand is 0.2 % (w/v).

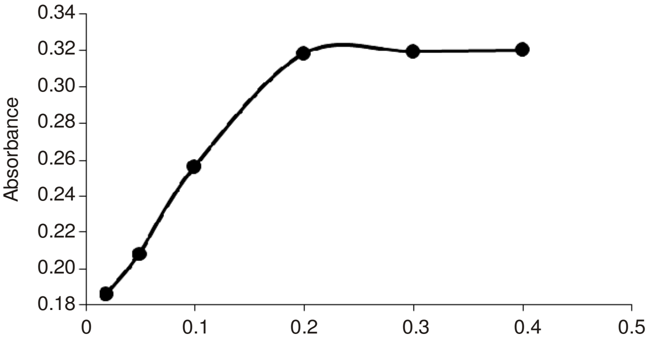


Fig. 4. Effect of ligand concentration

**Temperature:** The extraction of complex into the drop was performed in the range of 5-30 °C and the results show an optimum temperature of 20 °C and maximum efficiency was attained in this temperature (Fig. 5). At low temperatures the formation constant ($K_f$) of metal complex is decreased and at high temperatures, the partition coefficient in two phases and also the organic phase volume are decreased.

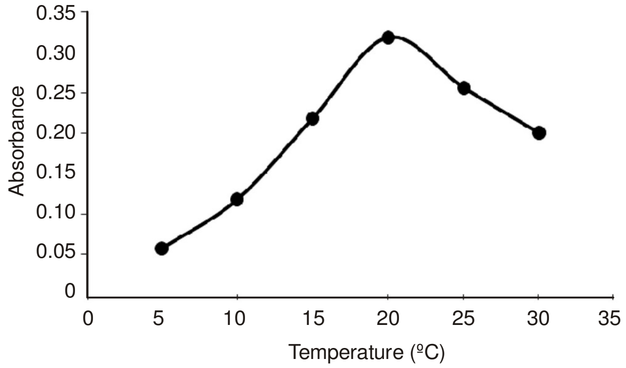


Fig. 5. Effect of temperature

**Extraction time:** The time of extraction was varied from 2-30 min. By increasing the extraction time, the extraction of bismuth complex into the drop is increased. However after 20 min the drop becomes saturated with the bismuth complex and the extraction efficiency attains constancy (Fig. 6). As the results show the optimum extraction time is 20 min.

**Volume of aqueous and organic phase:** Changing the organic volume from 1-4 μL increased the extraction efficiency. However higher volumes were avoided due to mechanical instability. 10 mL solution volume was chosen for the analysis as lower volumes caused falling of the drop due to agitation and higher volumes showed no benefit for the extraction process and were not used.

**Effect of ionic strength and salt concentration:** The effect of ionic strength was tested using potassium chloride in the concentration range of 0.02-0.25 mol $L^{-1}$ (Fig. 7).

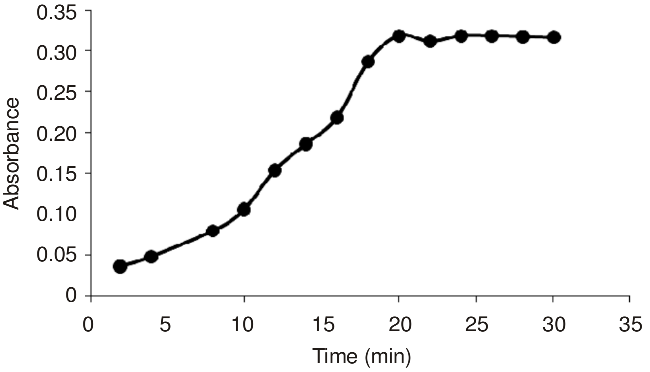


Fig. 6. Effect of time

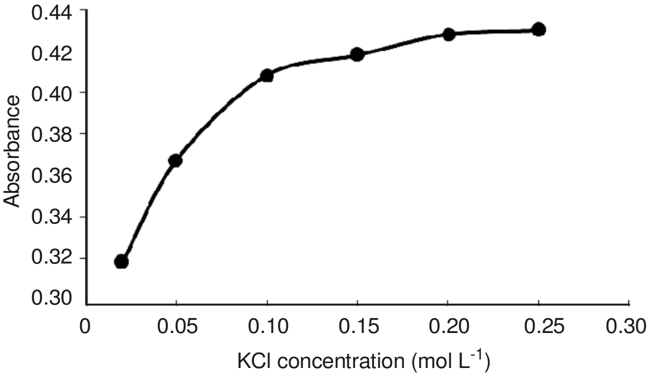


Fig. 7. Effect of ionic strength

At high concentrations of salt, solvent molecules are in contact with salt ions and Bi(III) ions are relatively free in the solution for complexion. By this action, the efficiency of extraction is increased but higher concentration of salt than 0.1 mol $L^{-1}$ decreases this effect and the extraction efficiency becomes constant.

**Effect of interferences:** Interfering species at 100 fold excess were added to Bi(III) solution and the extraction was followed at the optimized conditions. The following table shows the results (Table-2): The severe interferences are due to $Cd^{2+}$, $Hg^{2+}$, $Sb^{3+}$, $Ag^+$ and $Au^{3+}$ which could be effectively removed by using separate solutions of 0.1 M KCN for $Au^{3+}$, $Ag^+$, $Cd^{2+}$ and $Hg^{2+}$ and 0.1 M tartaric acid for $Sb^{3+}$.

TABLE-2
EFFECT OF INTERFERING IONS

| Interfering ion* | Relative error in absorbance (%) | Interfering ion* | Relative error in absorbance (%) |
|---|---|---|---|
| $Cl^-$ | -0.5 | $Sn^{4+}$ | -2.1 |
| $NO_3^-$ | 0.8 | $Sb^{3+}$ | -18.3 |
| $PO_4^{3-}$ | -1.3 | $Cr^{3+}$ | -0.2 |
| $SO_4^{2-}$ | 1.8 | $Cu^{2+}$ | 1.5 |
| $AsO_3^{3-}$ | -2.1 | $Hg^{2+}$ | -11.6 |
| $SiO_3^{2-}$ | -3.1 | $Pb^{2+}$ | 0.8 |
| $Na^+$ | 0.5 | $Fe^{3+}$ | -1.9 |
| $K^+$ | 1.5 | $Zn^{2+}$ | -4.8 |
| $Mg^{2+}$ | -1.8 | $Ag^+$ | -10.7 |
| $Ca^{2+}$ | 2.0 | $Mn^{2+}$ | -0.6 |
| $Cd^{2+}$ | -18.7 | $Co^{2+}$ | -0.9 |
| $Ba^{2+}$ | -1.6 | $Ni^{2+}$ | -3.8 |
| $Al^{3+}$ | -3.2 | $Au^{3+}$ | -21.8 |

*The solutions for cations is preparation of chloride salts and also anions preparation of sodium salts.

**Analytical figures of merit:** Calibration curve was constructed at the optimized conditions and was linear in the range of 19 pg mL$^{-1}$ to 2.4 ng mL$^{-1}$ bismuth with a correlation coefficient of 0.9998 and sensitivity of 4.0 pg mL$^{-1}$. The detection limit was calculated to be 19 pg mL$^{-1}$ based on 3S$_b$. The relative standard deviation (RSD) for five replicate analysis of 0.5 ng mL$^{-1}$ bismuth was 4.8 %. Recovery test was performed using tap water, waste water, sea water spiked with 0.5 ng mL$^{-1}$ bismuth and also soil sample spiked with 10 µg g$^{-1}$ bismuth. The results shows a recovery of 95-106 % for the technique.

## Application

**Analysis of real sample:** In order to evaluate the capability of the method, different real samples and reference materials were analyzed according to the method described earlier. The results are given in Tables 3 and 4.

TABLE-3
RESULTS OF DETERMINATION BISMUTH IN REAL SMAPLES

| Sample | Bi added (ng mL$^{-1}$) | Bi found (ng mL$^{-1}$) | Recovery (%) |
|---|---|---|---|
| Tap water | 0 | 0 | – |
| | 0.50 | 0.51 ± 0.08 | 102 |
| Waste water | 0 | 0.15 ± 0.05 | – |
| | 0.50 | 0.62 ± 0.06 | 95 |
| Sea water | 0 | 0.06 ± 0.03 | – |
| | 0.50 | 0.59 ± 0.05 | 105 |
| Soil sample | 0 | 10.1 µg g$^{-1}$ ± 0.1 | – |
| | 10.0 µg g$^{-1}$ | 21.3 µg g$^{-1}$ ± 0.3 | 106 |

TABLE-4
RESULTS OF DETERMINATION BISMUTH
IN REFERENCE MATERIALS

| Reference material | Reported value | Determination value | Recovery (%) |
|---|---|---|---|
| JSL-1 | 0.53 µg g$^{-1}$ | 0.52 µg g$^{-1}$ ± 0.07 | 98 |
| NCSDC73301 | 0.53 µg g$^{-1}$ | 0.54 µg g$^{-1}$ ± 0.09 | 102 |

## Conclusion

The results show a promising technique for determination of bismuth in a variety of samples at ng mL$^{-1}$ and pg mL$^{-1}$ levels without the needs for any sophisticated device. Apart from having extremely high sensitivity, the procedure is simple, nearly fast and benefits a very low detection limit. By the use of a preliminary separation step using a resin, the method could be relatively free from interferences. The experimental parameter such as chemical modifier, organic solvent, pH of aqueous phase, sampling temperature, extraction time, volume of aqueous and organic phase and ionic strength have great effects on the sensitivity of method and should be optimized. The results show that the bismuth could be determined with high sensitivity and relatively good reproducibility in aqueous samples such as tap water, sea water, waste water and solid samples.

## ACKNOWLEDGEMENTS

The authors thank Ferdowsi University of Mashhad for financial support of this work (No. P-207; dated June 2009).

## REFERENCES

1. R.L. Bertholf and B.W. Renoe, *Anal. Chim. Acta*, **139**, 287 (1982).
2. M. Burguera, J.L. Burguera, C. Rondon and M.I. Garcia, *J. Anal. At. Spectrom.*, **16**, 1190 (2001).
3. J.L. Burguera, M. Burguera, C. Rivas, C. Rondon, P. Carrera and M. Gallignani, *Talanta*, **48**, 885 (1999).
4. D.W. Thomas, T.F. Hartley, P. Coyle and S. Sobecki, Handbook on Toxicity of Inorganic Compounds, Marcel Decker, New York, p. 15 (1987).
5. D.W. Thomas, In ed.: E. Merian, Bismuth, Metals and their Compounds in the Environment, VCH, Weinheim, p. 789 (1991).
6. A.S. Ribeiro, M.A.Z. Arruda and S. Cadore, *Spectrochim. Acta B*, **57**, 2113 (2002).
7. O. Acar, Z. Kýlýç and A.R. Türker, *Anal. Chim. Acta*, **382**, 329 (1999).
8. L. Rahman, W.T. Corns, D.W. Bryce and P.B. Stockwell, *Talanta*, **52**, 833 (2000).
9. A. Morrow, G. Witshire and A. Huvsthous, *At. Spectrosc.*, **18**, 23 (1997).
10. L. Zhang, Y. Lu and G. Yang, *Huaxue Fenxe*, **36**, 26 (2000).
11. X. Feng and B. Fu, *Anal. Chim. Acta*, **371**, 109 (1998).
12. M.V. Hinds, D.C. Gregoie and E.A. Ozaki, *J. Anal. At. Spectrom.*, **12**, 131 (1997).
13. P. Ostapczuk, *Anal. Chim. Acta*, **273**, 35 (1993).
14. H.-Y. Yang, W.-Y. Chen and I.-W. Sun, *Talanta*, **50**, 977 (1999).
15. R.D. Ye and S.B. Khoo, *Electroanalysis*, **9**, 481 (1997).
16. C.M. Wang, Q.Y. Sun and H.L. Li, *Electroanalysis*, **9**, 645 (1997).
17. T. Ferri, S. Paci and R. Morabito, *Ann. Chim.*, **89**, 245 (1996).
18. R. Hajian and E. Shams, *Anal. Chim. Acta*, **491**, 63 (2003).
19. A. Alonso, M.J. Almendral, M.D. Báez, M.J. Porras, F. López Lavýn and C. Garcýa de Marýa, *Anal. Chim. Acta*, **408**, 129 (2000).
20. S.G. Sarkar and P.M. Dhadke, *Sep. Purif. Technol.*, **15**, 131 (1999).
21. J.M. Lo, Y.P. Lin and K.S. Lin, *Anal. Sci.*, **7**, 455 (1991).
22. N. Tokman, S. Akman and M. Ozcan, *Talanta*, **59**, 201 (2003).
23. Y. Yamini, M. Chaloosi and H. Ebrahimzadeh, *Talanta*, **56**, 797 (2002).
24. M.H. Pournaghi-Azar, D. Djozan and H.A. Zadeh, *Anal. Chim. Acta*, **437**, 217 (2001).
25. S. Moyano, J.A. Gasquez, R. Olsina, E. Marchevsky and L.D. Martinez, *J. Anal. At. Spectrom.*, **14**, 259 (1999).
26. J.B.B. Silva, M.B.O. Giacomelli and A.J. Curtius, *Analyst*, **124**, 1249 (1999).
27. E. Vassileva, L. Proinova and K. Hadjiivanov, *Analyst*, **121**, 697 (1996).
28. R. Kocjan and M. Garbacka, *Sep. Sci. Technol.*, **29**, 799 (1994).
29. F. Shemirani, M. Baghdadi, M. Ramezani and M.R. Jamali, *Anal. Chim. Acta*, **534**, 163 (2005).
30. R. Liu, P. Wu, K. Xu, Y. Lv and X. Hou, *Spectrochim. Acta*, **63B**, 704 (2008).
31. Z.-X. Li and Y.-A. Guo, *Talanta*, **65**, 1318 (2005).
32. M.T.H. Tarafder, K.-B. Chew, K.A. Crouse, A.M. Ali, B.M. Yamin and H.-K. Fun, *Polyhedron*, **21**, 2683 (2002).
33. N.R. Pramanik, S. Ghosh, T.K. Raychaudhuri, S. Ray, R.J. Butcher and S.S. Mandal, *Polyhedron*, **23**, 1595 (2004).