



## Synthesis and Characterisation of Phenanthroline Adducts of Pb(II) Complexes of *BisN*-alkyl-*N*-ethylthiocarbamates

NORMAH AWANG<sup>1</sup>, NADIA ATIQA NORDIN<sup>2</sup>,  
NURLINA RASHID<sup>2</sup> and NURUL FARAHANA KAMALUDIN<sup>3</sup>

<sup>1</sup>Environmental Health and Industrial Safety Programme, School of Diagnostic and Applied Health Sciences, Faculty of Health Sciences, Universiti Kebangsaan, Malaysia.

Jalan Raja Muda Abdul Aziz, 50300 Kuala Lumpur, Malaysia.

<sup>2</sup>School of Chemical Science and Food Technology, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia.

<sup>3</sup>Biomedical Science Programme, School of Diagnostic and Applied Health Sciences, Faculty of Health Sciences, Universiti Kebangsaan Malaysia, Jalan Raja Muda Abdul Aziz, 50300 Kuala Lumpur, Malaysia.

\*Corresponding author Email: awang\_normah@yahoo.com

<http://dx.doi.org/10.13005/ojc/310138>

(Received: December 20, 2014; Accepted: January 15, 2015)

### ABSTRACT

Dithiocarbamates are a class of metal-chelating compounds with various applications in medicine. They have been used for the treatment of bacterial and fungal infections, possible treatment of AIDS, and most recently cancer. Dithiocarbamates are well-known compounds to bind strongly and selectively to many metal ions. Dithiocarbamate ligands readily form chelates with metal ions through its two donor sulphur atoms. A new series of plumbum(II) complexes with mixed ligands, dithiocarbamate, and 1,10-phenanthroline were successfully synthesised using *in situ* method. Microelemental analysis data of the complexes were in agreement with the general formula,  $Pb[S_2CNR'R'']_3phen$  ( $R'$  = ethyl,  $R''$  = butyl, cyclohexyl; phen = 1,10-phenanthroline). Infrared spectra of the complexes showed that the thioureide  $\nu(C-N)$  band was in the region 1450–1500  $cm^{-1}$ . The unsplitting band of  $\nu(C-S)$  in the region 930–1000  $cm^{-1}$  indicated the bidentate nature of the chelated dithiocarbamate ligands. The  $^{13}C$  NMR chemical shift of the carbon atom of the  $N-CS_2$  group appeared in the range of 202–207 ppm.

**Key words:** Dithiocarbamate, Thioureide, Plumbum, Chemical shift, Phenanthroline.

### INTRODUCTION

Dithiocarbamates are highly versatile monoanionic chelating ligands that form stable complexes with all the transition elements and the majority of main group elements, lanthanide and

actinide elements (Hogarth 2012). Dithiocarbamates are prepared from primary or secondary amines. Depending upon the nature of the cation, dithiocarbamates can show good solubility in water or organic solvents. Dithiocarbamates are lipophilic and generally bind

to metals in a symmetrical chelate fashion. There are also other coordination modes, but monodentate and ambidentate modes are the two most prevalent ones.

Dithiocarbamates stabilise metals in a wide range of oxidation states, this being attributed to the existence of soft dithiocarbamate and hard thioureide resonance forms, the latter formally resulting from delocalisation of the nitrogen lone pair onto the sulphurs, and consequently their complexes tend to have a rich electrochemistry (Onwudiwe 2014). Tetraethyl thiuramdisulphide (disulfiram or antabuse) has been used as a drug since the 1950s, but it is only recently that dithiocarbamate complexes have been explored within the medicinal domain. Over the past two decades, anticancer activity of gold and copper complexes has been noted. Technetium and copper complexes have also been used in PET imaging. Copper complexes have also been investigated as SOD inhibitors. Other than that, dithiocarbamates have been used to treat acute cadmium poisoning.

Tetrahedral metal dithiocarbamate complexes are known to expand their coordination numbers by adding neutral nitrogen ligands. The crystal structure on mixed ligand complexes involving cadmium dithiocarbamate with nitrogen bidentate ligand, 1,10-phenanthroline has been reported (Lai *et al.* 2003; Ali *et al.* 2009). All the adducts contain discrete molecular units with  $\text{CdS}_4\text{N}_2$  chromophore in a distorted octahedral geometry.

In our previous work, we have reported several compounds and adduct of dithiocarbamate complexes (Awang *et al.* 2011; Awang *et al.* 2010). As an extension of this research, here we report the synthesis of two new Pb(II) dithiocarbamate compounds, which are  $\text{Pb}[\text{S}_2\text{CN}(\text{C}_2\text{H}_5)(\text{C}_4\text{H}_9)]_2$  (compound 1) and  $\text{Pb}[\text{S}_2\text{CN}(\text{C}_2\text{H}_5)(\text{C}_6\text{H}_{11})]_2$  (compound 2). We also report their adducts, which are  $\text{Cd}[\text{S}_2\text{CN}((\text{C}_2\text{H}_5)(\text{C}_4\text{H}_9))]_2(\text{phen})$  (compound 3) and  $\text{Cd}[\text{S}_2\text{CN}(\text{C}_2\text{H}_5)(\text{C}_6\text{H}_{11})]_2(\text{phen})$  (compound 4), together with their elemental analysis and spectroscopic characterisation.

## MATERIALS AND METHOD

### Reagents

Secondary amines (*N*-butyl-*N*-ethylamine and *N*-cyclohexyl-*N*-ethylamine) and ethanol (95%) were obtained from Fluka Chemical. Carbon disulphide and methanol (99.5%) were from Ajax Chemical Ltd., and dichloromethane (99.5%) from R & M Chemical (99.5%).  $\text{PbCl}_2$  chloride was purchased from Merck. All the chemicals were used as supplied without purification.

### Synthesis of dithiocarbamate compounds

#### Synthesis of Plumbum(II) *N*-alkyl-*N*-ethyl dithiocarbamate Compounds (Compound 1 and 2)

Compound 1 and 2 were synthesised by the method given by Thirumaran *et al.* (1998) with some modifications. Carbon disulphide (30 mmol) in ethanol was slowly added to an ethanolic solution of *N*-alkyl-*N*-ethylamine (30 mmol). The reaction temperature was controlled under 4°C. The mixture was stirred about 1h, and a pale yellow solution formed. After that, 30 mmol of plumbum(II) chloride in ethanol solution was added, and the yellowish precipitate was obtained. The precipitate was filtered and washed with cold ethanol. The reaction scheme for the above preparation is given in Figure 1.

#### Synthesis of Plumbum(II) *N*-alkyl-*N*-ethyl dithiocarbamate (Phen) Compounds (Compound 3 and 4)

Compound 3 and 4 were prepared by adding equimolar of compound 1 or compound 2 and bidentate nitrogen ligand (1,10-phenanthroline) in the mixture of ethanol and chloroform solutions. The resulting mixture was stirred for 1 h and allowed to evaporate at room temperature. The pale yellow precipitate formed and was washed with cold ethanol and dried *in vacuo*. The reaction scheme to synthesise compounds 3 and 4 is shown in Figure 2.

### Physical measurements

Elemental analysis (CHNS) was carried out on a CHNS/O Fison Model EA 1108 elemental analyser. Melting points were determined using an Electrothermal 9100 instrument. The infrared spectra were recorded on a Perkin Elmer FT-IR Model SpectrumGX spectrophotometer; using KBr discs for the wavenumber range between 4000 and

400  $\text{cm}^{-1}$  and nujol in polyethylene tablets for the wave number range between 400 and 250  $\text{cm}^{-1}$ . The  $^{13}\text{C}$  NMR spectra were recorded using a Jeol JNM-LA 400 spectrometer with TMS as the internal standard.

## RESULTS AND DISCUSSION

### Physical and Elemental Analysis

The synthesised compounds were solid and stable in air. The elemental analysis and melting

point data for the title compounds are given in Table 1. Elemental analysis was done to compare the observed values with predicted values of percentage of the carbon, hydrogen, nitrogen, and sulphur. The elemental analysis data were in good agreement with the expected values. These data showed that the chemical formula for the compound 1 and 2 was  $\text{Pb}[\text{S}_2\text{CN}(\text{CH}_2\text{CH}_3)(\text{R})]_2$  ( $\text{R} = \text{C}_6\text{H}_{11}$  or  $\text{C}_4\text{H}_9$ ), whereas for compound 3 and 4 was  $\text{Pb}[\text{S}_2\text{CN}(\text{CH}_2\text{CH}_3)(\text{R})]_2 \cdot \text{C}_{12}\text{H}_8\text{N}_2$  ( $\text{R} = \text{C}_6\text{H}_{11}$  or  $\text{C}_4\text{H}_9$ ). The proposed structures for compound 1 and

Table 1: Results of elemental analysis of compound 1 to 4

Cpd.	Chemical Formula	C (%)	H (%)	N (%)	S (%)	Melting point(°C)
1	$\text{Pb}[\text{S}_2\text{CN}(\text{CH}_2\text{CH}_3)(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)]_2$	29.06 30.04	5.28 5.00	4.94 5.04	18.51 22.91	77.1–77.6
2	$\text{Pb}[\text{S}_2\text{CN}(\text{CH}_2\text{CH}_3)(\text{C}_6\text{H}_{12})]_2$	36.19 35.21	4.93 5.58	5.03 4.56	21.26 20.89	155.0–157.2
3	$\text{Pb}[\text{S}_2\text{CN}(\text{CH}_2\text{CH}_3)(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)]_2 \cdot \text{C}_{12}\text{H}_8\text{N}_2$	41.50 42.19	2.37 2.68	5.03 4.90	16.24 17.33	117.0–120.4
4	$\text{Pb}[\text{S}_2\text{CN}(\text{CH}_2\text{CH}_3)(\text{C}_6\text{H}_{12})]_2 \cdot \text{C}_{12}\text{H}_8\text{N}_2$	41.83 42.77	4.87 4.10	6.60 7.12	15.08 10.87	168.2–169.7

Note: Cpd: Compound

Table 2: Infrared spectra data of important bands for compound 1 to 4

Cpd.	Chemical Formula	C-H	C=N <sub>aromatic</sub>	C-N	C=C	C-S	Pb-N	Pb-S
1	$\text{Pb}[\text{S}_2\text{CN}(\text{CH}_2\text{CH}_3)(\text{C}_4\text{H}_9)]_2$	2932	-	1452	-	989	-	369
2	$\text{Pb}[\text{S}_2\text{CN}(\text{CH}_2\text{CH}_3)(\text{C}_6\text{H}_{12})]_2$	2932	-	1468	-	984	-	370
3	$\text{Pb}[\text{S}_2\text{CN}(\text{CH}_2\text{CH}_3)(\text{C}_4\text{H}_9)]_2 \cdot \text{C}_{12}\text{H}_8\text{N}_2$	2927	1618	1406	1407	989	431	374
4	$\text{Pb}[\text{S}_2\text{CN}(\text{CH}_2\text{CH}_3)(\text{C}_6\text{H}_{12})]_2 \cdot \text{C}_{12}\text{H}_8\text{N}_2$	2930	1556	1448	1411	985	419	373

Note: Cpd: Compound

2 are shown in Figure 2. All the compounds were nonhygroscopic and stable at room temperature. These compounds were insoluble or sparingly soluble in most common organic solvent and quite soluble in chloroform. They had sharp melting point. The small range of their melting point showed that these compounds had a good purity (Awang *et al.* 2010).

### Infrared Spectroscopy

The characteristic infrared absorption frequencies ( $\text{cm}^{-1}$ ) and assignment of important

absorption bands of the compound 1 to 4 are listed in Table 2. The significant absorptions in the dithiocarbamate complexes mainly are due to the  $\nu(\text{C-N})$  and  $\nu(\text{C-S})$  stretching modes (Geeta and Thirumaran 2008). The  $\nu(\text{C-N})$  was used as a measure of the contribution of the thioureide group to the structure of the dithiocarbamate. The  $\nu(\text{C=N})$  appeared at an intermediate value between the two extremes of 1250–1350  $\text{cm}^{-1}$  and (1650–1690  $\text{cm}^{-1}$ ) (Baggio *et al.* 1992). IR spectra of the complexes showed that the shift of the thioureide bands to lower frequencies compared to the parent

Table 3:  $^{13}\text{C}$  NMR spectra data ( $\delta$ , ppm) for compound 1 to 4

Cpd.	Chemical Formula	$\text{N}^{13}\text{CS}_2$	$-\text{C}_\alpha\text{H}_2\text{C}_\beta\text{H}_3$	R ( $\text{C}_4\text{H}_9$ or $\text{C}_6\text{H}_{11}$ )	$\text{C}_{12}\text{H}_8\text{N}_2$
1	$\text{Pb}[\text{S}_2\text{CN}(\text{CH}_2\text{CH}_3)(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_2]$	202.32	$\text{C}_\alpha$ :47.85, $\text{C}_\beta$ :12.28	52.50, 29.18, 20.31, 13.88	-
2	$\text{Pb}[\text{S}_2\text{CN}(\text{CH}_2\text{CH}_3)(\text{C}_6\text{H}_{12})_2]$	201.99	$\text{C}_\alpha$ :42.53, $\text{C}_\beta$ :14.41	61.70, 30.39, 25.76, 25.41	-
3	$\text{Pb}[\text{S}_2\text{CN}(\text{CH}_2\text{CH}_3)(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_2] \cdot \text{C}_{12}\text{H}_8\text{N}_2$	207.08	$\text{C}_\alpha$ : 47.83, $\text{C}_\beta$ : 12.25	52.48, 29.15, 20.29, 13.85	150.40, 146.33, 136.09, 128.72, 126.61, 123.17
4	$\text{Pb}[\text{S}_2\text{CN}(\text{CH}_2\text{CH}_3)(\text{C}_6\text{H}_{12})_2] \cdot \text{C}_{12}\text{H}_8\text{N}_2$	202.09	$\text{C}_\alpha$ : 42.48, $\text{C}_\beta$ : 14.36	61.76, 30.45, 25.81, 25.48	153.75, 147.69, 132.52, 121.97, 119.68, 113.81

Note: Cpd: Compound

bisdithiocarbamate was due to the increase in coordination number around the metal ion (Awang *et al.* 2011, Manohar *et al.* 2012). The thioureide band was well differentiated from the ring frequencies associated with N-donors, which were observed in the  $1600\text{--}1500\text{ cm}^{-1}$ . The  $\nu(\text{C-S})$  bands appear around  $990\text{ cm}^{-1}$  in all the complexes without any splitting, supporting the bidentate coordination of the dithiocarbamate moiety (Manohar *et al.* 1998). Figure 1(a-b) shows the IR spectra of compound 1 and 3.

The  $^{13}\text{C}$  NMR spectra data of compound 1

to 4 are shown in Table 34. The assignments of –CSS group in the investigated compounds were straight ward as observed in the range of 201.99–207.08 ppm, indicating the coordination of sulphur to the lead atom. The  $\text{N}^{13}\text{CS}_2$  chemical shift was the most important signal in the  $^{13}\text{C}$  NMR spectra for the dithiocarbamate compounds. The  $^{13}\text{C}$  NMR spectra of compound 3 and 4 were observed at 207.08 and 202.09 ppm, respectively, which shifted to downfield compared to the parent compound (compound 1 and 2). The shift could be explained by an increase of  $\sigma$ -bond order in the whole  $\text{NCS}_2$  moiety. This means that the chelation of the bidentate

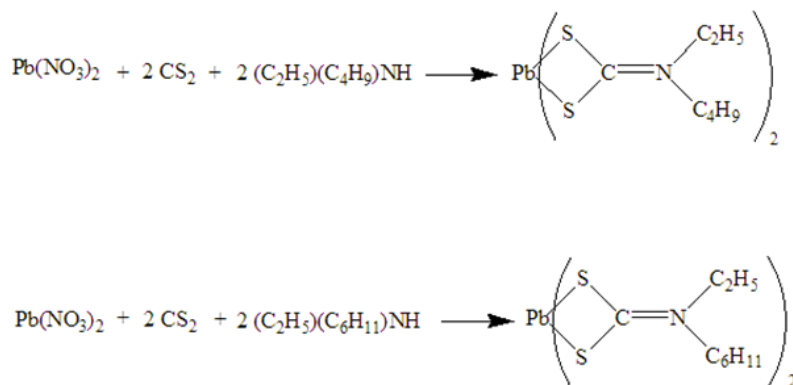
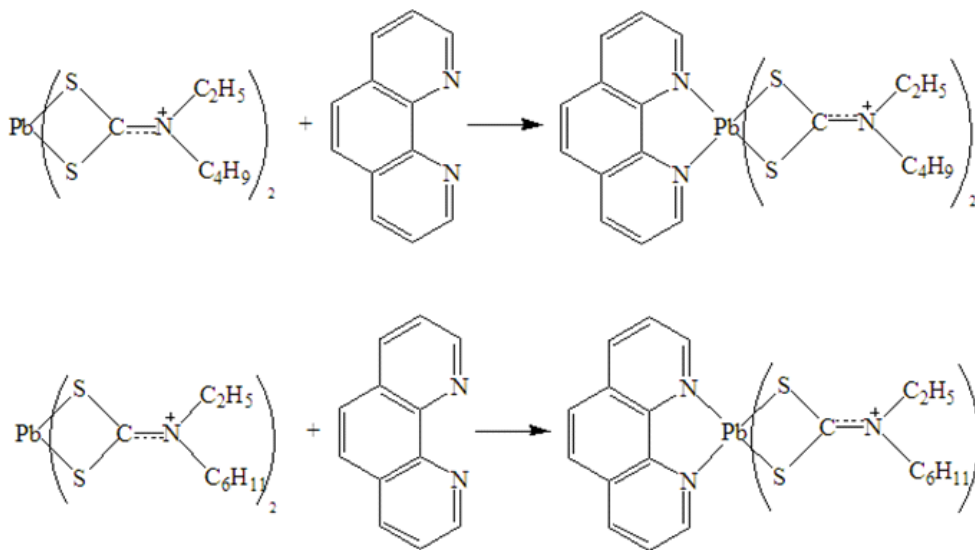


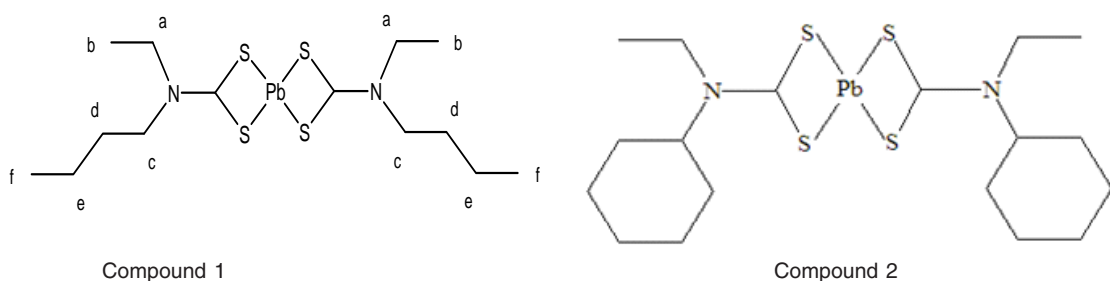
Fig. 1: Reaction scheme between *N*-alkyl-*N*-ethylamine, carbon disulphide, and plumbum(II)nitrate

nitrogen ligands to the plumbum atom promoted the delocalisation of the unshared electron pair in the nitrogen atom in the dithiocarbamate group (Awang *et al.* 2011). The occurrence of six resonances in the range of 123–151 and 113–154

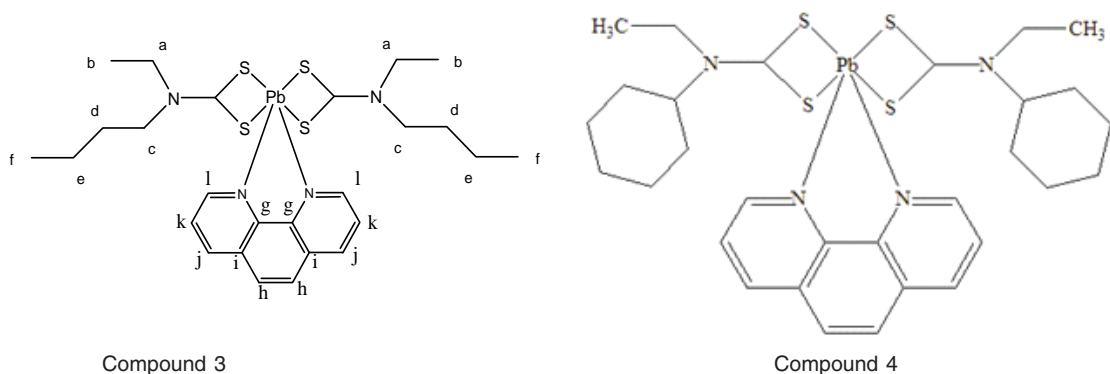
ppm for compound 3 and compound 4, respectively, was defined as benzene carbon signals of 1,10-phenanthroline ligand. Meanwhile, the signals of ethyl group ( $C_{\alpha}$  and  $C_{\beta}$ ) were seen in the range of 12.25–47.85 ppm.



**Fig. 2:** Reaction scheme between plumbum(II) *N*-alkyl-*N*-ethyldithiocarbamate with 1,10-phenanthroline



**Fig. 3:** Proposed structure of compound 1 and 2



**Fig. 4:** Proposed structure of compound 3 and 4

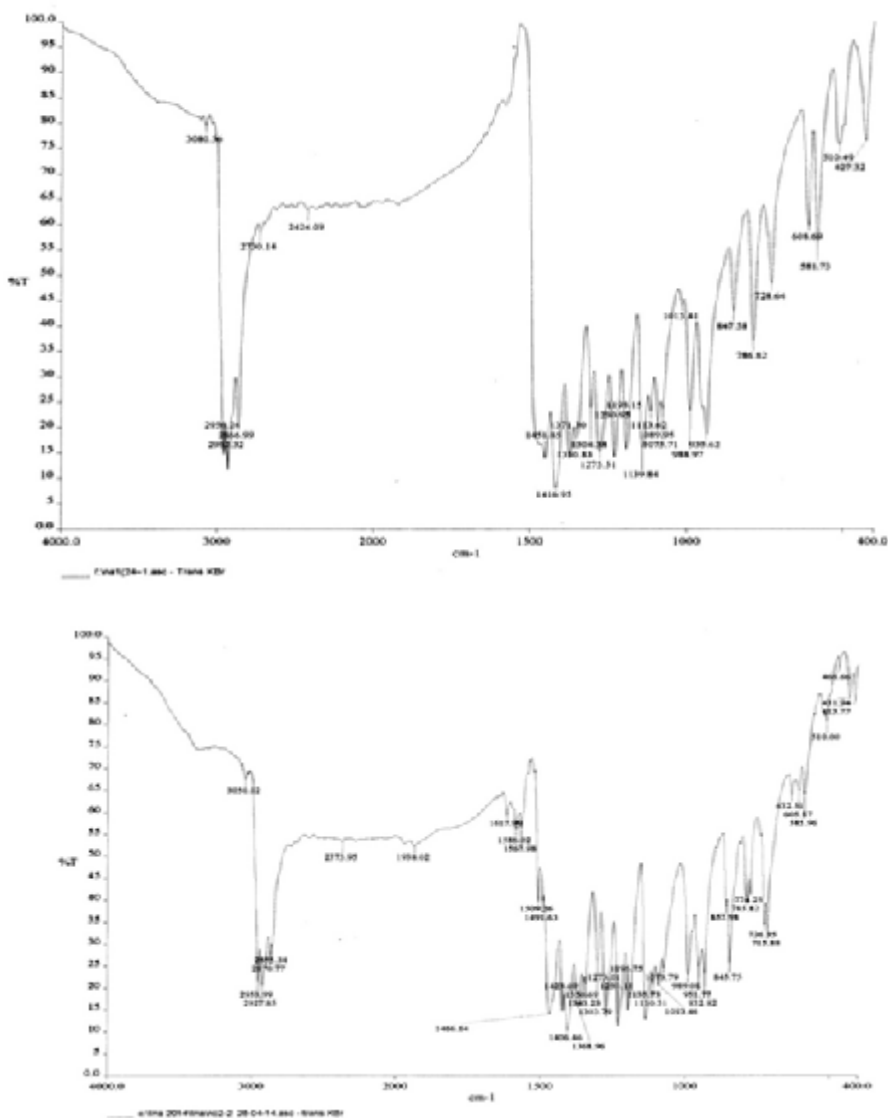


Fig. 5: IR spectra of compound 1 (a) and compound 3 (b)

## CONCLUSION

The parent plumbum(II) dithiocarbamate and their nitrogenous adduct have been successfully synthesised and characterised. The IR spectra data of the compounds showed that the thioureide band values were lower than the values observed for the parent dithiocarbamate compounds. A reduction in the thioureide stretching frequency was due to the increase in coordination around the cadmium ion and the resultant increase in electron density.

## ACKNOWLEDGEMENTS

We would like to thank the Malaysia Ministry of Higher Education for the financial support (Grant Code:06-01-02-SF0887). We would also like to thank for technical support from the laboratory assistants of Faculty Science and Technology, Universiti Kebangsaan Malaysia.

## REFERENCES

1. Manohar, A., Ramalingam, K. Karpagavel, K. &Kulandisamy, A. *International Journal of ChemTech Research*. **2012**, 4(3): 1023-1032.
2. Hogarth, G. Metal-dithiocarbamate complexes: chemistry and biological activity. *Mini Rev. Med. Chem.* **2012**, 12(12): 1202-1215.
3. Lai, C.S. and Tiekink, E.R.T. Bis(N, N-ditehtyldithiocarbamato)(2,9-dimethyl-1,10-phenanthroline) cadmium(II). *Appl. Organometalic Chem.* **2003**, 17: 139-140.
4. Ali, B.F., Al-Far, R., Zaghal, M.H., Judeh, Z. and Haddad, S.F. Cadmium(II) diallyldithiocarbamate complexes with 2,2'-bipyridine and 1,10-phenanthroline: Spectroscopic and crystal structure analysis. *J. Coord. Chem.* **2009**, 62: 2028-2036.
5. NormahAwang, Ibrahim Baba, Bohari M. Yamin and Azhar Abdul Halim. Preparation, Characterization and Antimicrobial Assay of 1,10-Phenanthroline and 2,2'-Bipyridyl adducts of Cadmium(II) N-Sec-Butyl-NPropyldithiocarbamate: Crystal Structure of  $Cd[S_2CN(i-C_4H_9)(C_3H_7)]_2(2,2'-Bipyridyl)$ . *World Applied Sciences Journal* **2011**, 12(9): 1568-1574.
6. NormahAwang, Ibrahim Baba, Bohari M. Yamin and SeikWeng Ng. Bis(N-isobutyl-N-propyl-dithiocarbamat- $\kappa^2$  S,S')zinc(II). *Acta Crystallographica Section E: Structure Reports Online*. **2010**, 66(2):m215.
7. Manohar, A., Venkatachalam, V., Ramalingam, K. Thirumaran, DS. Bocelli, G. &Cantoni, A. Synthesis, spectral, and single crystal X-ray structural studies on (2,2'-bipyridyl)bis(dimethyldithiocarbamato)zinc(II) and (1,10-phenanthroline) bis(dimethyldithiocarbamato)zinc(II), *Journal of Chemical Crstallography*. **1998**, 28(12): 861-866.
8. Onwudiwe, D.C., Arfin, T. and Strydom, C.A. Fe(II) and Fe(III) Complexes of N-Ethyl-N-Phenyldithiocarbamate: Electrical Conductivity Studies and Thermal Properties. *ElectrochimicaActa*, **2014**, 127:283-289.
9. Geetha, N. &Thirumaran, S. Characterization studies and cyclic voltammetry on nickel(II) amino acid dithiocarbamates with triphenylphosphine in the coordination sphere. *J. Ser. Che. Soc.* **2008**, 73(2): 169-177.
10. Thirumaran, S., V. Venkatachalam, A. Manohar, K. Ramalingam and G. Bocelli.. Synthesis and characterization of bis(N-Methyl-N-ethanol-dithiocarbamato)M(II) (M = Zn, Cd, Hg) and Bis(N,N-(iminodiethylene)-bisphthalimidedithiocarbamato)M(II) (M = Zn, Cd, Hg) complexes. Single crystal X-ray structure of bis(di(2-hydroxyethyl)-dithiocarbamato)zinc(II). *J. Coord. Chem.*, **1998**, 44: 281-288.